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Sources of Halogenated Hydrocarbons in an Urban Water Supply

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New Brunswick, NJ

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16. ABSTRACT

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a) general stream survey;
b) sewage treatment plant effluent survey;
c) industrial waste treatment plant effluent survey;
d) source, finished and delivered drinking water survey.

This extensive portion of the survey - monitoring effort was perfomed through the grant period. Intensive sampling programs centered around the variation of halogenated material contained in both raw and finished drinking water processed at the Passaic Valley Treatment Plant, located in Little Falls, New Jersey. Several intensive studies were conducted using short and long sampling frequencies. It was observed that resulting halogenated hydrocarbon concentrations varied to a greater extent when a smaller sampling period was employed. Additional investigations of the trihalomethane formation potential and rate of tribhalomethane production for stream samples were performed.

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by

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Grant No. R804394

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FOREWORD

The Environmental Protection Agency was created because of increasing public and government concern about the dangers of pollution to the health and welfare of the American people. Noxious air, foul water, and spoiled land are tragic testimony to the deterioration of our natural environment. The complexity of that environment and interplay between its components require a concentrated and integrated attack on the problem.

Research and development is that necessary first step in problem solution and it involves defining the problem, measuring its impact, and searching for solutions. The Municipal Environmental Research Laboratory develops new and improved technology and systems for the prevention, treatment, and management of wastewater and solid and hazardous waste pollutant discharges from municipal and community sources, for the preservation and treatment of public drinking water supplies, and to minimize the adverse economic, social, health, and aesthetic effects of pollution. This publication is one of the products of that research; a most vital communications link between the researcher and the user community.

The presence of halogenated organics in water supplies and the formation of certain halocarbons has been recognized as one of our major water quality problems. In this publication, the results of research on the sources and nature of such halocarbons in a highly urbanized watershed are presented.

Francis T. Mayo, Director
Municipal Environmental Research
Laboratory

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ABSTRACT

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a) general stream survey;

b) sewage treatment plant effluent survey;

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This report was submitted in fulfillment of the conditions of EPA Grant No. R804394 by the Department of Environmental Science, Rutgers University, under the sponsorship of the U.S. Environmental Protection Agency. This report covers the period May 1, 1976 through January 15, 1980.

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SECTION 1

INTRODUCTION

The results of the National Organic Reconnaissance Survey (NORS) conducted by EPA (Symons, et al., 1975) startled members of the water treatment community and indicated contamination of raw and finished drinking waters throughout the U.S. by chlorinated and brominated methanes and ethanes. Halogenated organics may be present in the raw water supply or be formed during the chlorination of water in water treatment plants. Water supplies receiving significant amounts of treated waste waters, combined sewer overflow and storm water runoff would be expected to contain substantial quantities of the precursors of halogenated organics formed during treatment as well as the halogenated organics that are actual contaminants of storm or waste waters or in a smiliar fashion formed in wastewaters during disinfection before discharge.

The purpose of the present study was to investigate the extent of contamination of the Passaic River by halogenated organic compounds and to determine the influence of chlorination at a drinking water treatment plant on the concentration of halogenated material in the finished water. The nature, source, concentration, distribution and variation of halogenated organics in the water supply and its potential to form additional halogenated organics during chlorination will indicate the procedures required to reduce the contamination levels of the finished water.

The Passaic River in northern New Jersey was selected as the study area as it represents one of the major water supplies of this part of the State. The region is highly urbanized, and the river receives substantial waste water pollution, as can be observed from Table 1.

TABLE 1. TOTAL DAILY VOLUME OF TREATED WASTE WATER DISCHARGED TO THE PASSAIC RIVER WATERSHED

Receiving Water	Discharge, gallons
Upper Passaic River	16,165,000
Rockaway River	7,850,000
Whippany River	14,968,000
Pequannock-Pompton Rivers	4,057,000
Wanaque River	423,000
Ramapo River	3,024,000
From the Two Bridges to Little Falls	5,718,000
Total Daily Volume	52,205,000

A map of the Passaic River Watershed is presented in Figure 1. The sampling stations are shown on this map and are detailed in Table 2. Those taken at the Passaic Valley Water Commission Treatment Plant at Little Falls, New Jersey, are so designated.

TABLE 2. STREAM SAMPLE LOCATIONS AND DESIGNATIONS

Station Number	Location
100	Passaic River Main Intake, Little Falls
106-B	Singac Brook at Two Bridges, Wayne
110	Singac Brook at Two Bridges, Fairfield
115	Delaval Brook, Fairfield
120	Passaic River at Bloomfield Ave. Bridge, Pine Brook
130	Passaic at Eagle Rock Ave. Bridge, Roseland
140	Passaic at Rt. 10 Bridge, Livingston
150	Passaic River at Passaic Ave. Bridge, Chatham
160	Passaic River at Rt. 24 Bridge, Chatham
165	Passaic River at Stanley Ave. Bridge, Chatham
170	Passaic River at River Road Bridge, Summit
175	Passaic River at Passaic Ave. Bridge, New Providence
180	Passaic River at Maple Ave., Davis Bridge, Basking Ridge
200	Whippany River Series
210	Whippany R. at Edwards Rd., Parsippany-Troy Hills
220	Whippany R. at Troy Rd. Bridge, East Hanover
221-B	Black Brook above its confluence with the Whippany River, East Hanover
225	Whippany River at Mellanie Rd., East Hanover
230	Whippany River at Rt. 10 Bridge, Whippany
240	Whippany River at Whippany Rd. Bridge, Whippany
250	Whippany River at St. Thomas St. Bridge, Whippany
260	Whippany River at Jefferson Rd., Whippany
270	Whippany River at Park Ave. Bridge, Cedar Knolls
280	Whippany River at Hanover Ave. Bridge, Morristown

(continued)

TABLE 2 (continued)

Station Number	Location
285	Whippany River below Whippany Paper Board Plant
290	Whippany River at Speedwell Ave. Bridge, Morristown
300	Rockaway River Series
310	Rockaway River at Rt. 46 Bridge, Montville
320	Rockaway River at Changebridge Rd., Montville
321-B-3	Crooked Brook at Fulton St., a tributary of the Rockaway River at Boonton
330	Rockaway River at Beverwick Rd. Bridge
340	Rockaway River at Breenkank Rd. Bridge, Boonton
350	Rockaway River at Morris Ave. above Boonton Reservoir, Boonton
400	Pequannock River Series
410	Pequannock River at Hamburg Turnpike Bridge, Riverdale
420	Pequannock River at Bridge, rear of Sloan Park, Bloomingdale
421-B	Kikeout Brook, before confluence with Pequannock River, Butler
430	Pequannock River at Main St. Bridge, Butler
440	Pequannock River under Rt. 23 Bridge, Butler
450	Pequannock River at Milopin Intake near Rt. 23
500	Wanaque River Series
510	Wanaque River at Hamburg Turnpike Bridge, Pompton Lakes
520	Wanaque River at Wanaque Ave. Bridge, Pompton Lakes
530	Wanaque River at Ringwood Ave. Bridge, below Wanaque Dam, Wanaque
540	Post Brook upstream of Twin Lakes
600	Pompton River Series
610	Pompton River at Two Bridges, Fairfield
620	Pompton River at Rt. 202 Bridge, Lincoln Park
630	Pompton River at Rt. 23 Bridge, Pequannock
640	Pompton River at Newark Pompton Turnpike Bridge, Pequannock

(continued)

TABLE 2 (continued)

Station Number	Location
650	Pompton River at Jackson Ave. Bridge, Wayne
660	Pompton River at Dawes Ave. Bridge, Pompton Lakes
670	Pompton River at Hamburg Turnpike Bridge, Pompton Lakes
700	Ramapo River Series
705	Ramapo River at Pompton Lakes Dam
710	Ramapo River at Pleasureland, Oakland
720	Ramapo River at Skyline Drive, Oakland
725	Ramapo River at intersection Rt. 202, Rt. 17
730	Ramapo River at Glen Gray Rd., Ramapo, N. Y.
740	Ramapo River at Cleveland Bridge, Darlington
750	Ramapo River at Jersey Ave. Bridge, Suffern, N. Y.
755	Masonic Brook Rt. 202 Mahwah
760	Ramapo River at Harriman Lane, Harriman, N. Y.
800	Dead River Series
805	Dead River
810	Dead River at King George Rd., Mt. Bethel

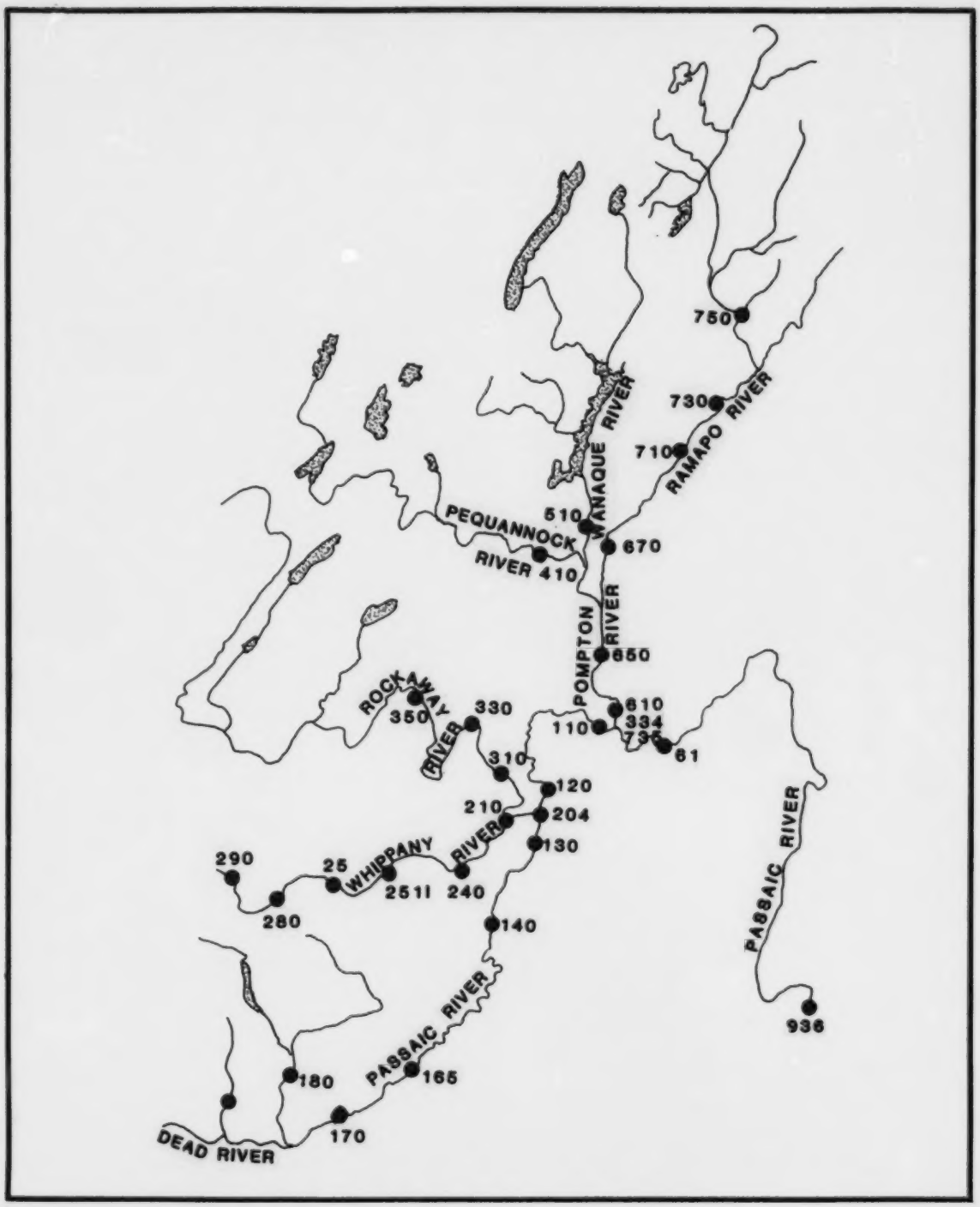

Figure 1. The Upper Passaic River Basin.

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SECTION 2

CONCLUSIONS

1. During summer months, chloroform was the dominant volatile halogenated organic compound detected in the Passaic River or its tributaries.

2. During colder months, under ice cover, methylene chloride was the dominant volatile halogenated organic compound detected in the Passaic River or its tributaries.

3. Additional volatile halogenated organic compounds detected in the Passaic River above Little Falls, New Jersey, at the 0.1 to 10 µg/1 range included the following: 1,1,1-trichloroethane, 1,1,2,2-tetrachloroethylene, bromodichloromethane, 1,1,2-trichloroethane, 1,1,2,2-tetrachloroethane and dibromomethane.

4. Polychlorinated biphenyls, such as Arochlor 1242, were frequently observed at concentrations less than 20 µg/1 in the Passaic River. A point source of Arochlor 1242 was found and the discharge eliminated.

5. Frequently observed organochlorine pesticides in the study (stream and discharge samples) were α and β-BHC. On one occasion, a significant concentration of heptachlorepoxide was observed in a discharge sample.

6. One set of stream samples and finished water samples revealed that trichlorophenol had the greatest distribution followed by 2,4-dichlorophenol, 2,6-dichlorophenol, tetrachlorophenol and pentachlorophenol.

7. During a one week intensive monitoring program of the Passaic River at Little Falls, the greatest variation in volatile halogenated hydrocarbons was observed for non trihalomethane compounds indicating up stream intermittent discharges.

8. A number of unidentified electron capturing components were present in extracts obtained from stream samples especially for the Ramapo River.

9. The trihalomethane formation potential (THMFP) of stream samples were in the range of 66 to 282 µg/1 total trihalomethanes (TTHM).

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10. Instantaneous total trihalomethane concentrations for the two finished and source waters treated at the Passaic Valley Water Commission (Passaic River source and the Wanaque Reservoir source) were of similar magnitude. The Wanaque supply did show a greater TTHMFP at the time tested.

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SECTION 3

RECOMMENDATIONS

After an assessment of the data obtained during the course of this grant activity and the evaluation of trends present in the data collected, the following set of recommendations directed specifically towards the protection of water quality and enhancement of the quality of potable water are advanced:

1) A routine schedule of watershed monitoring should be required to control the discharge of halogenated materials that enter the water treatment facility at Little Falls.

2) The characterization of industrial and municipal discharges on the watershed.

3) The institution of simple and rapid test procedures to insure the quality of raw and finished waters.

4) Monitoring of treatment modification, such as disinfectant application, to minimize THM formation.

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SECTION 4

PROCEDURES

A. SAMPLING

Because of the volatile nature of many of the halogenated organics, grab samples rather than composited samples were collected. Pyrex, teflon-sealed bottles that had been washed, rinsed with distilled water, rinsed with pesticide grade acetone and heated overnight at 250°C were used to collect samples. The containers were always completely filled with sample to avoid volatiles losses. The samples were placed in an ice chest and returned immediately to the laboratory for analysis. When it was necessary to prevent further action of oxidants in chlorinated waters, the samples were collected in bottles containing one gram of sodium thiosulfate.

B. PREPARATION OF CARBON FILTERED WATER

Normal tap water contains far too many halogenated components to be considered as a reagent for use in a recovery or blank sample preparation. Conventional distilled water concentrates the more volatile materials in distillate and is also unacceptable. Several methods of removing volatile halogenated materials from aqueous solution have been employed, they are the following: boiling, vacuum degassing, sparging with an inert gas, and use of an adsorbent such as polymeric resin or activated carbon. Each method has its own particular merits and disadvantages.

1. Boiling distilled water removes a great deal of volatile halogenated hydrocarbons but this is time consuming and presents storage problems. In addition, this procedure is not adequate to remove high boiling halogenated hydrocarbons quantitatively.

2. Vacuum degassing suffers from many of the same drawbacks as a boiling procedure.

3. Sparging distilled water with an inert gas (i.e., He) removes volatile halogenated hydrocarbons quantitatively but requires a great deal of time (24 hours for 20 ℓ), and product water has only a limited shelf life. Additionally, this procedure does not remove high boiling organochlorine pesticides, PCB's, and toxaphene.

4. Activated carbon requires a great deal of preparation (i.e., HCl washing, elutriation of fines and conditioning at high temperatures for activation), but once prepared the material can be stored until ready for use. Activated carbon columns are prepared (3.25 m x 50 mm id) and distilled water is used as the feed. This procedure removes both volatile and high boiling halogenated materials (see attached chromatograms) efficiently. Blank water samples are run on a schedule as noted.

C. PREPARATION OF EXTERNAL STANDARDS FOR VOLATILE ORGANIC ANALYSIS

1. Gaseous Components

Vinyl chloride, fluoroform, methyl chloride and methyl bromide are all gases at room temperature. A stock solution for each is prepared by the following procedure:

a. Place 100 ml of methyl alcohol into a 100 ml volumetric flask.

b. Weigh the apparatus and record the weight. (This is the initial weight.)

c. Connect a lecture bottle of the desired gas to a pipet and place the gaseous stream below the alcohol level in the flask and initiate flow at approximately 10-20 ml/min.

d. Allow gas flow to continue for 15-20 minutes.

e. Remove the gas flow.

f. Adjust the alcohol volume to 100 ml, weigh, and record the weight. (This is the final weight.)

g. Obtain the concentration of the gases as follows:

$$\text{Gas Concentration (mg/ml)} = \frac{\text{Final Weight (mg)} - \text{Initial Weight (mg)}}{100 \text{ ml}}$$

h. Transfer stock solution to Teflon capped septa vials and store at 4°C until ready for use.

i. Discard the used vial.

2. Liquid Components

Methyl chloride, chloroform, 1,2-dichloroethane, 1,1,1-trichloroethane, carbontetrachloride, 1,1,2-trichloroethylene, dichlorobromomethane, 1,1,2-trichloroethane, dibromochloromethane, 1,2-dibromoethane, 1,1,2,2-tetrachloroethylene, bromoform, 1,1,2,2-tetrachloroethane, diiodomethane, m-dichlorobenzene, p-dichlorobenzene, o-dichlorobenzene, and 1,3,5-trichlorobenzene, all

have boiling points in excess of 40°C and are prepared as liquid standards (except p-dichlorobenzene which is a solid) in the following manner:

a. Tare a 100 ml volumetric flask on a top loading balance (accurate to 1 mg).

b. Add each component (the range is 0.5 to 15 grams depending on the component) to the flask and record the component weight. Bring the flask to a volume of 100 ml by the addition of n-pentane. Determine the concentration of each component in ug/ul as follows:

$$\text{Component Concentration (ug/ul)} = \frac{\text{Sample Weight in mg}}{100 \text{ ml}}$$

c. Dilute stock solution 100 times to prepare a working solution that will have a concentration range of 0.5-15 ug/ul (in methyl alcohol).

3. Preparation of Calibration Standards

a. Calibration Standards

1) Add gaseous and liquid components combined in working stocks to 100 ml of carbon filtered water contained in a 150 ml Teflon lined screw top sampling bottle.

2) Utilize the liquid-liquid extraction procedure for sample preparation.

b. Comparison Solutions

1) Add the same dosage of components as applied to the 100 ml water sample to 10 ml of n-pentane. Place this solution into a 1 ml septum vial and run as a sample.

2) Obtain the recovery value for each component as follows:

$$\% \text{ Recovery} = \frac{\text{Area of Component from Calibration Standard}}{\text{Area of Component from Standard Solution}} \times 100$$

3) Use calibration standards to calibrate the gas chromatographic system.

D. DETERMINATION OF VOLATILE HALOGENATED ORGANIC COMPOUNDS

During the course of the project, several changes were made in the methodologies for the determination of the volatile organohalogen compounds. The methods employed for the analysis of these compounds are presented in detail later in the text; but briefly, the methods used were: purge and trap using a Hall electrolytic conductivity detector, liquid-liquid extraction with n-pentane using packed gas chromatography column and an electron capture detector, and liquid-liquid extraction with n-pentane in conjunction with

glass capillary column chromatography and an electron capture detection.

1. Purge and Trap Method

Inert gas purging of an aqueous solution was performed using a Tekmar liquid sample concentration, Tekmar, Inc., Cincinnati Ohio, similar in principle to the method proposed by Bellar and Lichtenberg (1974). While purging the volatile materials from solution, the effluent gas stream is passed over an adsorbent column that exhibits selectivity for halogenated species. The trap material consists of 2/3 tenax g.c. + 1/3 silica gel type 15. The trap column is thermally desorbed and the gas evolved is swept onto the head of an analytical gas chromatographic column at 40°C. Detection of compounds in the G.C. column effluent is by use of a halogen specific Hall model 700 electrolytic conductivity detector (Tracor Inst., Austin, Texas). A typical volatile halogenated hydrocarbon separation for purge and trap procedure is shown on the chromatogram in Figure 2.

A change in purging temperature to 80°C enhanced the transfer of volatile materials to the gas phase reducing the purge time by 70%. An overall reduction in analysis time from 72 to 32 minutes was produced by an additional modification: the reduction of analytical column length. However, the time savings was offset by a reduction in chromatographic resolution. A sample chromatogram obtained by the elevated temperature purge technique is shown in Figure 3. Enhancement in calibration plot linearity was obtained by this method especially for CCl_4 and CCl_2CCl_2.

Minimum detectability for both gas purging techniques, utilizing a Hall Model 700 Detector is within the range of 0.1 to 1.0 ppb for the following volatile halogenated organic compounds:

1. CH_2Cl_2
2. $CHCl_3$
3. CH_3CCl_3
4. CCl_4
5. $CHCl_2Br$
6. $CHClBr_2$
7. CCl_2CCl_2
8. $CHBr_3$
9. $CHCl_2CHCl_2$
10. $1,2\text{-}Cl_2C_6H_4$
11. $1,2,4\text{-}Cl_3C_6H_3$

Both purging techniques exhibited adequate sensitivity for most applications to raw and finished waters, the shortcoming of the method is the difficulty in converting to an automated technique, which is desirable for many laboratory applications.

2. Pentane Extraction Followed by Packed Column Gas Chromatography

A pentane extraction preparation technique was found most desirable in that it decreased analysis time to 20 minutes for the trihalomethanes and enhanced the limits of detection for most compounds by a factor of ten or more. This technique also is preferable for automated analysis. The limitation for extraction when using packed columns and an electron capture detector is a decrease in the number of halogenated hydrocarbons than can be detected. This is due to isothermal column operation. Thus, the halobenzenes are

Figure 2. Ambient purge and trap chromatogram of ten volatile organic compounds.

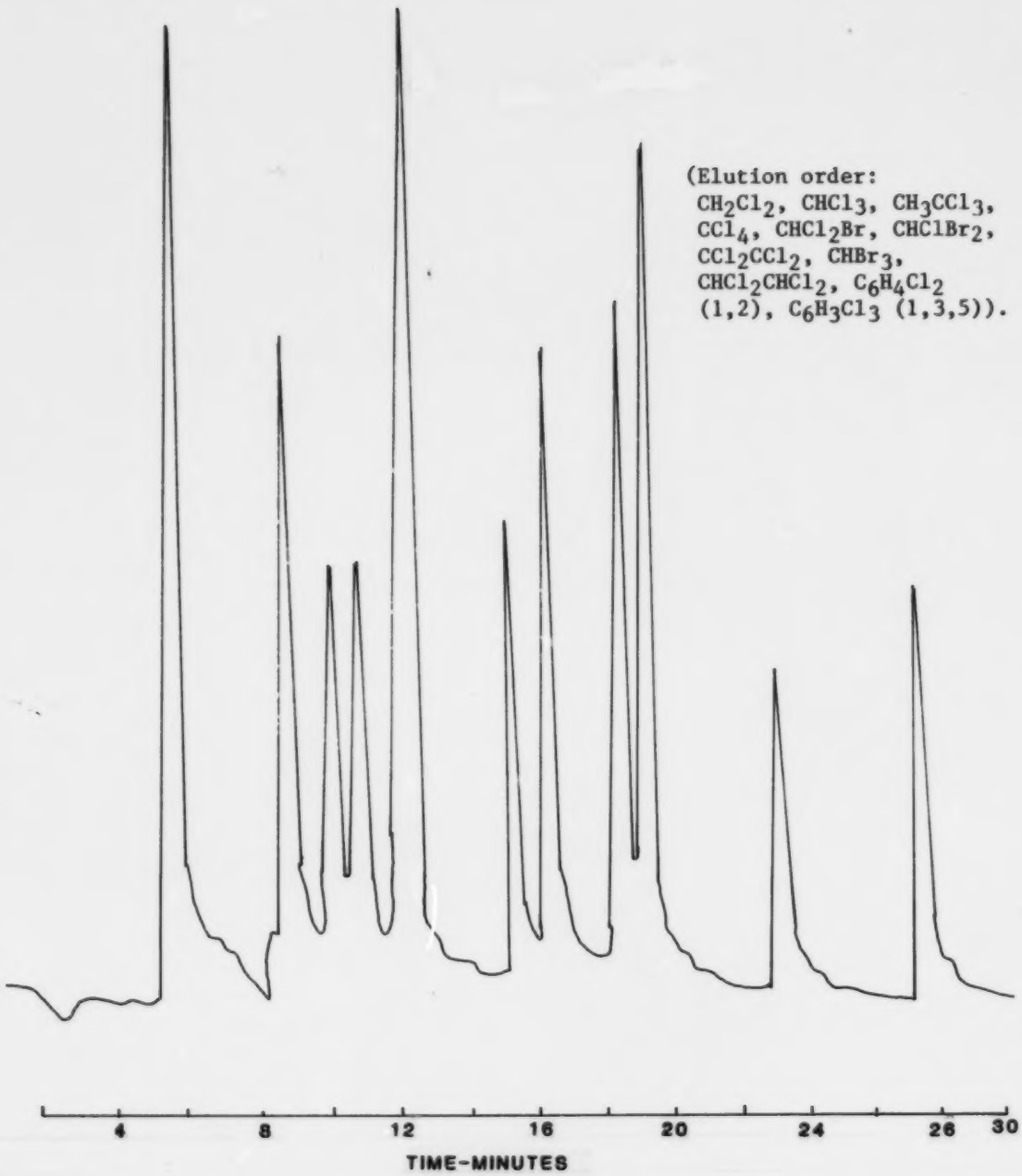

Figure 3. Chromatogram from elevated temperature purge and trap procedure for eleven volatile halogenated hydrocarbons.

eluted from the column only after a long period of time (55 mins. for trichlorobenzene) because of their high boiling points. This situation may be considered a handicap by some but many advantages are apparent and are listed in the discussion below. A typical standard mixture separation is shown in Figure 4.

Column materials for volatile halogenated hydrocarbon separation were selected from the literature and narrowed to the following:
Tenax g.c. 60/80 mesh - porous polymer, Chromosorb 101 and 102 - porous polymers, Carbopack C + 0.1% SP1000 (60/80 mesh), and 20% SP2100 + 0.1% CW 15M, 100/120 mesh Supelcoport.

Tenax g.c. proved adequate but when temperature programmed using a Hall 700 Detector above 200°C, bleed became a problem. Chromosorbs 101 and 102 are similar to Tenax g.c. and were not evaluated because similar bleed problems were anticipated. Carbopack C + 0.1% SP1000 produced undesirable tailing when coupled to a Hall Detector and temperature programmed. In addition degradation of resolution ensued in only a short period of time (1-2 weeks). Carbopack C + 0.1% SP1000 was thus deemed undesirable. Twenty percent (20%) SP2100 + 0.1% CW 15M on 100/120 Supelcoport proved successful for resolution of many components and remained efficient after long periods of use.

a. Extraction Procedure

The technique used for the isolation of volatile halogenated hydrocarbons is based on a liquid-liquid extraction procedure (LLE). The chlorinated materials of interest were partitioned into n-pentane and the solvent layer was removed and placed in a septum sealed vial. A microliter volume was then injected into a gas chromatograph operating under isothermal conditions. An electron capture detector was used for selective response. The procedure is outlined as follows:

1) Collect the aqueous sample in a 100 ml sample bottle with a Teflon-lined screw top. Reduce any free residual chlorine by the addition of $Na_2S_2O_3$.

2) Add a 50 ml aliquot of the aqueous samples to a 25 x 200 mm test tube with a Teflon-lined screw top. Layer 5 ml of n-pentane atop the aqueous layer.

3) Agitate the solvent/sample mixture on a Burrell shaker for three (3) minutes.

4) After the layers have separated, remove the n-pentane layer with a Pasteur pipet. Transfer the n-pentane layer to a 10 ml septum bottle with a Teflon-lined septa.

5) Inject a 5 ul aliquot of the n-pentane extract into a gas chromatograph equipped with an electron capture detector.

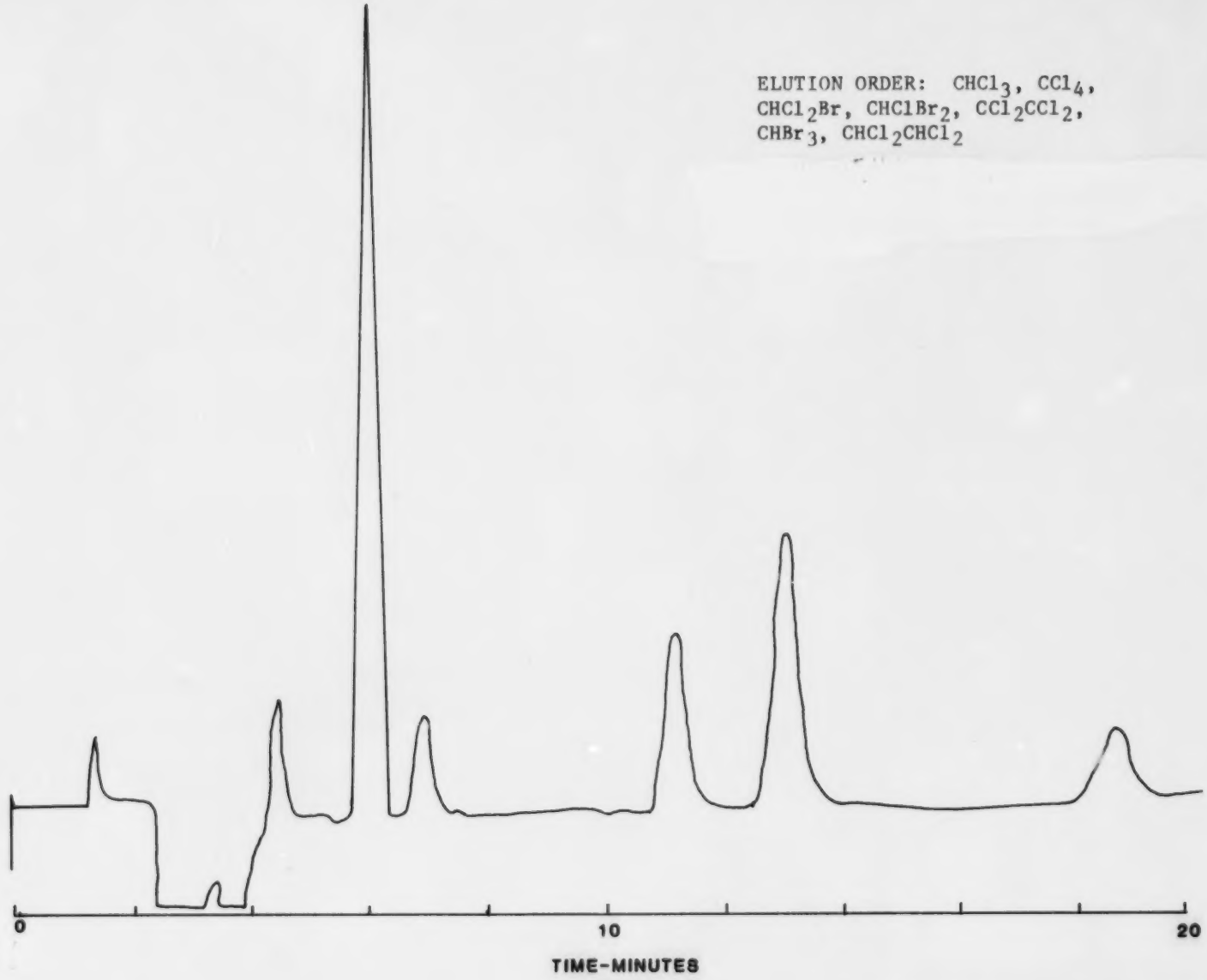

Figure 4. Chromatogram from pentane extraction procedures for seven volatile halogenated hydrocarbons.

Recovery studies have indicated that the following compounds have extraction efficiencies in the range of 88-98%: $CHCl_3$, CH_2Cl-CH_2Cl, CH_3CCl_3, CCl_4, $CHCl_2Br$, $CHCl-Br_2$, CH_2Br-CH_2Br, $CCl_2{=}CCl_2$, $CHBr_3$, and $CHCl_2{=}CHCl_2$.

Some solute peaks overlap and coelute as one chromatographic peak. The following compounds fall into this group: $CHCl{=}CCl_2$ and $CHCl_2Br$.

b. Precision and Accuracy

The method of calibration utilizes a calibration standard. By taking this approach, the need to correct for recovery is unnecessary. Control of deviation in calibration runs is selected by the operator. A 10% window was used, that is, if calibration factors are ± 10% of the data already in the microprocessor of the gas chromatograph, these data are stored and an update calibration factor is calculated. Data outside the 10% window are not used for calibration factor calculation.

Accuracy of the method for a 0.6 to 3.3 ppb mixed standard is illustrated in Table 3.

TABLE 3. ACCURACY OF EXTRACTION/PACKED COLUMN GC PROCEDURE FOR VOLATILE HALOGENATED ORGANICS (n = 7)

Compound	Amount Added ppb	Amount Found ppb	Deviation %
$CHCl_3$	1.49	1.47	- 1.3
CH_2ClCH_2Cl	1.26	1.30	+ 3.2
CCl_3CH_3	1.35	1.34	- 0.7
CCl_4	1.59	1.57	- 1.3
$CHCl_2Br$	0.61	0.61	0
$CHCl_2CHCl_2$	2.87	2.88	+ 0.4
$CHClBr_2$	1.00	1.00	0
CH_2BrCH_2Br	2.18	2.09	- 4.1
$CCl_2{=}CCl_2$	1.62	1.61	- 0.62
$CHBr_3$	2.89	2.94	+ 1.7
$CHCl_2CHCl_2$	1.60	1.51	- 5.6
CH_2I_2	3.33	3.50	+ 5.1

c. Minimum Reportable Concentrations

The limiting factor in reporting sensitivity information for this group of compounds is the contamination of the extracting solvent and the carbon filtered (water blank) with compounds under investigation. After analyzing a number of commercially available n-pentane stocks, it was found that Fisher certified grade contained the least amount of contamination.

Minimum reportable concentrations for volatile halogenated hydrocarbons are shown in Table 4.

TABLE 4. DETECTION LIMITS FOR EXTRACTION/PACKED COLUMN GC PROCEDURE FOR VOLATILE HALOGENATED ORGANICS

Compound	Minimum Detectable Level ppt
$CHCl_3$	50
CH_2ClCH_2Cl	100
CH_3CCl_3	50
CCl_4	20
$CHCl_2Br$	50
$CHCl_2CH_2Cl$	300
$CHClBr_2$	50
CH_2BrCH_2Br	100
CCl_2CCl_2	50
$CHBr_3$	100
$CHCl_2CHCl_2$	200
CH_2I_2	300

d. Precision and Accuracy of Method

The purging method used at the beginning of this project exhibited precision in the range of ± 10-20% for all of the standard compounds. The accuracy was not measured for this technique. The precision and accuracy of the n-pentane extraction technique is shown in Table 5 and recovery data shown in Table 6. For gas chromatographic systems with automatic data handling capabilities, recovery runs can be used to calibrate the data system. The procedure can be modified for analysis of sludge and effluent samples which are difficult to perform by the purging technique.

TABLE 5. PRECISION AND ACCURACY OF EXTRACTION/PACKED COLUMN GC PROCEDURE FOR SELECTED VOLATILE HALOGENATED ORGANICS

Run Number	Concentration, ppb						
	$CHCl_3$	CCl_4	$CHCl_2Br$	$CHClBr_2$	CCl_2CCl_2	$CHBr_2$	$CHCl_2CHCl_2$
1	14.73	16.21	14.70	14.42	16.62	28.81	15.91
2	14.80	17.13	15.67	14.07	17.47	27.46	15.28
3	13.98	15.61	13.91	13.66	15.62	27.55	15.27
S.D. ppb	0.45	0.77	0.88	0.38	0.93	0.76	0.37
% Coefficient variation	3.1	4.7	6.0	2.7	5.6	2.7	2.4
True Value	14.97	15.99	14.80	14.50	16.23	18.89	15.85
± % Error	-3.1	+1.9	-0.3	+3.1	+2.1	-3.3	-2.3

TABLE 6. RECOVERY DATA FOR N-PENTANE EXTRACTION PROCEDURE FOR VOLATILE HALOGENATED HYDROCARBONS (BASED ON PEAK HEIGHT)

Compound	Percent Recovery (for triplicate analyses)
$CHCl_3$	88
CCl_4	98
$CHCl_2Br$	100
$CHClBr_2$	90
CCl_2CCl_2	97
$CHBr_3$	88
$CHCl_2CHCl_2$	100

3. Pentane Extraction Followed by Capillary Column Gas Chromatography

As the study progressed, the need for better resolution of the volatile halogenated organic peaks during gas chromatography became apparent. Therefore, a capillary column procedure was developed. The details of the procedure are in the following section.

a. Procedure Details

1) Remove 50 ml of sample from the 150 ml sampling bottle by carefully pouring it into a graduated cylinder.

2) Using a 10 ml volumetric pipet, add 10 ml of pentane to the sample bottle.

3) Recap the bottle tightly and shake the bottle for one minute. This assures the complete mixing of pentane and the sample water.

4) Allow the water and pentane layers to separate. An emulsion may form in some samples, especially surface water samples. The emulsion is characterized by small bubbles in the pentane layer and must be centrifuged, as outlined below, before the pentane extract is chromatographed.

   a) Rinse two centrifuge tubes with pentane and let them air dry.

   b) Using a Pasteur pipet, draw off the pentane layer and put equal amounts in each tube. Make sure all the emulsion layer is removed. Small quantities of water can be present in the tubes since it will be separated.

   c) Centrifuge the mixture for two minutes (or longer; check the tubes periodically) until the emulsion is gone and two distinct layers of pentane and water are present.

5) Using a Pasteur pipet, remove the pentane layer from the bottle (or centrifuge tubes) and pipet it into the four corresponding 1.75 ml vials. Seal the vials.

   a) Make sure no water is transferred to the vials.

   b) If any seals are damaged or the septum bulges at the top, reseal the vial.

b. Gas Chromatographic Analysis

1) Operating Conditions

   a) Capillary column - 60 m x 0.25 mm (i.d.) SP2100 or equivalent (i.e., OV101).

b) Inlet - open sleeve 2 mm (i.d.) for splitless injection.

c) Injector temperature = 130°C.

d) Linear carrier velocity = 45 cm/sec (H_2).

e) Temperature program profile initial temperature = 40°C.
5°C/min. from t = 7 min. to t = 19 min.
10°C/min. from t = 19 min. to t = 21 min.
Hold at 140°C from t = 21 min. to t = 27 min.

f) Splitless time delay = 0.5 min.

g) Detector utilized is 8 mc N^{63} electron capture using a pulsed 50 V.D.C. power supply.

2) Run Programming

Twenty-two halogenated compounds are determined in the n-pentane extract of each sample. The specific compounds are listed as follows: fluoroform (CHF_3), methyl chloride (CH_3Cl), methyl bromide (CH_3Br), vinyl chloride ($CH_2{=}CHCl$), methylene chloride (CH_2Cl_2), chloroform ($CHCl_3$), 1,2,-dichloroethane (CH_2ClCH_2Cl), 1,1,1-trichloroethane (Cl_3CCH_3), carbon-tetrachloride (CCl_4), 1,1,2-trichloroethylene ($CHCl{=}CCl_2$), dichlorobromo-methane ($CHCl_2Br$), 1,2-dibromoethane (CH_2BrCH_2Br), 1,1,2,2-tetrachloroethy-lene ($CCl_2{=}CCl_2$), bromoform ($CHBr_3$), 1,1,2,2-tetrachloroethane ($CHCl_2CHCl_2$), diiodomethane (CH_2I_2), 1,2-dichlorobenzene, 1,4-dichlorobenzene ($C_6H_4Cl_2$), 1,2-dichlorobenzene, 1,2,5-trichloroethane ($CHCl_2CH_2Cl$), dibromochloro-methane ($CHClBr_2$).

3) Method of Quantitative Analysis

An external standard calibration and quantification procedure is employed for the analyses of volatile halogenated hydrocarbons. This proce-dure is generally the most accurate procedure for quantification when used in conjunction with an automatic liquid sampler (ALS). Its prime advantage in the quantitation of unknown samples is that the reported analytical values are <u>absolute</u>, not relative, quantities.

4) Calibration Factors

Any quantitative method relies on the calculation of a calibration factor. For this method, the calibration factor is defined as follows:

$$\text{Calibration Factor (C.F.)} = \frac{\text{Component Concentration}}{\text{Component Area (X E-4)}}$$

Once each calibration factor is obtained (this involved a multiple calibra-tion and averaging of calibration factors at the outset of a bulk of analy-ses), it is a simple matter to determine sample component concentrations:

$$\text{CF} \times \text{Component Area X E-4} = \text{Component Concentration}$$

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This calculation is performed automatically and assumes the following:

a) That the component is correctly identified; i.e., within ± 2.5% retention time window for chloroform, retention time = 4.67 min. must be in the window 4.54-4.80 min. in order to be identified as chloroform and quantified.

b) That the detector response is linear near the point of calibration and below that point. In practice, most halogenated materials that are analyzed exhibit a large linear dynamic range; but to be certain of the quantitative information, two calibration points (usually the higher calibration is 5 to 10 times that of the lower) are determined. The analysis report thus contains two quantitative reports and the results are selected that fall into one of the calibration ranges. In some cases of extreme contamination, dilution of the sample is necessary to have the actual sample amount fall within the desired range.

5) Internal Quality Control

Internal quality control consists of several phases:

a) Calibration of data system and generation of calibration factors.

b) Analysis of procedural blanks (using carbon filtered water) to subtract from analytical results.

c) Analysis of n-pentane solvent blanks to determine if solvent purity is satisfactory.

d) Analysis of both low and high concentration calibration standards as unknowns in order to construct quality control charts. The schedule for the above, based on the number of samples analyzed, is as follows:

Internal Quality Assurance Phase	% Required
Calibration	10
Procedural blank	10
Solvent	as required
Unknown	10

In addition to the in-house quality assurance requirements, EPA quality assurance samples (VOA) in two concentration ranges were analyzed in replicate.

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6) Sensitivity, Precision and Recovery

Percent recovery information is presented along with precision data for a set of multiple runs for the 21 compounds in Tables 7 and 8. Similar information for procedural blanks (n-pentane extracted carbon filtered water) is shown in Table 9. A reasonable approach to the determination of the minimum detectable quantity of each compound is based on the evaluation of the blank value for that compound and the precision of the overall procedure for that specific material. The results of this evaluation of minimum detectable quantities is presented in Table 10. The method was then checked against EPA quality assurance samples, and the results are presented in Table 11.

E. DETERMINATION OF HIGH BOILING ORGANOCHLORINE COMPOUNDS

1. Liquid-Liquid Extraction Procedure

Two methods were used for the analysis of high boiling organochlorine pesticides and PCB's in natural waters. The first method employed was that recommended by U.S.E.P.A. in NPDES Appendix A (Fed. Reg. 38, #75, Pt. II). The only deviation from the recommended procedure was that the column material for GLC differed from those suggested. The column consisted of 1.95% SP2401 + 1.5% SP2250 on Supelcoport 100/120 mesh (Supelco Company, Bellefronte, Pa.). Each sample processed by this method was examined for the following common group of organochlorine pesticides: α-BHC, β-BHC, Heptachlor, Heptachlor epoxide, p,p'-DDE, Dieldrin, o,p'-DDD, and p,p'-DDT.

Minimum detectability for most pesticides using a 500 ml initial water sample ranged from less than one to approximately 10 parts per trillion. Electron capturing components present in the solvent did not interfere with the determination of pesticides or PCB's. The one interfering peak encountered eluted earlier than chromatographic peaks of interest. The minimum detectability for PCB's (based on Arochlor 1242) is approximately 0.05 ppb.

2. Steam Distillation Method Analysis for High Boiling Chlorinated Organic Compounds

The method used for the analysis of this group of chlorinated materials is based on an exhaustive steam distillation extraction procedure. The water sample is subjected to steam distillation, the distillate is extracted in the same appartus with a non-polar solvent. The finished solvent extract is contained in a small volume, thus there is little need for further concentration. Sensitivities for chlorinated pesticides are in the range of 10-200 parts per trillion. Chlorinated biphenyls, because they are a mixture, exhibit poorer sensitivities. Typical minimum detectability for Arochlor 1254 is on the order of 100 parts per trillion. Sensitivities for lower Arochlor mixtures (e.g., 1016 or 1242) vary about the 100 ppt level for this method. Two procedures were employed.

TABLE 7. RECOVERY AND STANDARD DEVIATION
FOR LOW LEVEL CALIBRATION (n=7)

Compound	Concentration Added ug/l	Standard Deviation ug/l	Recovery %
Fluoroform	4.00	0.27	74
Methyl Chloride	4.00	---	--
Methyl Bromide	4.00	0.51	52
Vinyl Chloride	4.00	0.23	65
Methylene Chloride	40.04	---	--
Chloroform	4.06	0.08	88
1,2-dichloroethane	30.06	0.83	77
1,1,1-trichloroethane	2.06	0.89	78
Carbon Tetrachloride	0.96	0.06	93
1,1,2-trichloroethylene	4.20	0.14	92
Dichlorobromomethane	1.40	0.05	89
1,1,2-trichloroethane	16.00	0.40	90
Dibromochloromethane	2.30	0.05	92
1,2-dibromoethane	2.20	0.05	90
1,1,2,2-tetrachloroethylene	1.05	0.03	93
Bromoform	16.16	0.54	94
1,1,2,2-tetrachloroethane	4.12	0.16	94
Diiodomethane	4.20	0.14	95
m-dichlorobenzene	16.10	0.64	98
p-dichlorobenzene	10.80	0.55	100
o-dichlorobenzene	16.00	1.10	93
1,3,5-trichlorobenzene	4.00	0.27	80

TABLE 8. RECOVERY AND STANDARD DEVIATION FOR VOLATILE HALOGENATED HYDROCARBON ANALYSIS (HIGH CALIBRATION) (n=7)

Compound	Concentration ug/l	Standard Deviation ug/l	Recovery %
Fluoroform	20.00	2.71	70
Methyl Chloride	20.00	2.88	67
Methyl Bromide	20.00	1.80	52
Vinyl Chloride	20.00	1.69	65
Methylene Chloride	400.4	102	18
Chloroform	40.60	2.01	81
1,2-dichloroethane	300.4	9.97	79
1,1,1-trichloroethane	20.60	1.27	99
Carbon Tetrachloride	9.60	0.44	92
1,1,2-trichloroethylene	42.00	2.38	90
Dichlorobromomethane	14.00	0.62	92
1,1,2-trichlorethane	160.00	7.23	85
Dibromochloromethane	23.00	1.07	93
1,2-dibromoethane	22.00	1.12	89
1,1,2,2-tetrachloroethylene	10.10	0.56	88
Bromoform	161.6	4.57	97
1,1,2,2-tetrachloroethane	41.20	1.94	92
Diiodomethane	42.00	2.12	94
m-dichlorobenzene	161.00	7.91	95
p-dichlorobenzene	108.00	5.64	93
o-dichlorobenzene	160.00	9.31	97

TABLE 9. TYPICAL PROCEDURAL BLANK ANALYSIS

Compound	Concentration ug/l
Methylene Chloride	44.80
Chloroform	0.38
1,1,1-trichlorethane	0.97
Carbontetrachloride	0.06
1,1,2,2-tetrachlorethylene	0.02
1,3,5-trichlorobenzene	0.97

TABLE 11. EPA QUALITY ASSURANCE SAMPLES FOR VOLATILE ORGANIC ANALYSIS #WS1276. PERFORMED BY N-PENTANE LLE WITH 60m-CAPILLARY COLUMN AND ELECTRON CAPTURE DETECTOR

COMPOUND	SAMPLE VOA - 1		SAMPLE VOA - 2	
	Found ug/l	True ug/l	Found ug/l	True ug/l
Chloroform	8.23±0.50	9.13	66.1 ±2.48	68.46
1,2-dichloroethane	1.75±0.15	1.39	28.55±0.58	27.21
1,1,1-trichloroethane	------	---	7.20±1.25	11.19
Carbontetrachloride	1.75±0.13	1.68	12.50±0.34	12.57
1,1,2-trichloroethylene	------	---	18.24±0.54	18.97
Dichlorobromomethane	1.18±0.05	1.19	11.05±0.36	11.90
Dibromochloromethane	2.72±0.13	2.74	17.59±0.92	17.15
Perchloroethylene	------	---	11.50 0.63	8.76
Bromoform	2.95±0.19	2.85	15.03±0.85	14.24

+ Average of three runs per sample

a. Initial Procedure

The isolation procedure employed for the chlorinated pesticides and PCB's was as follows:

1) 0.8 liter of sample was placed into a 1 liter conical flask, an ebbulator rod added to enhance bubble formation.

2) The condenser was charged with toluene (5 ml), and the sample was distilled for one hour.

3) After cooling, the interior of the apparatus was washed with 3 ml of toluene. The washings plus the extract were removed and brought to an 8 ml volume in a 10 ml graduated cylinder.

4) Toluene extracts were clean enough to be directly injected into a gas chromatograph fitted with an electron capture detector.

The analog data was reduced by a Varian CDS 111 data system. Recovery data in Table 12 indicates the distillation extraction efficiencies.

b. Final Procedure

The above method was altered to improve the recovery of the first three compounds listed in Table 12. In addition, toxaphene and methoxychlor were also included in the study. The details of the procedure follow.

1) Materials

a) Carbon filtered water (blank water) was obtained in a fashion similar to that described in the Procedure for Volatile Organic Compounds.

b) Equipment and Reagents

(1) Large scale steam distillation/extraction apparatus
(2) One liter conical flasks with 24/40 t/s joints
(3) Glass rod boil easers
(4) Ten ml graduated cylinders
(5) One ml vials and Teflon seals
(6) Pasteur pipets
(7) Stop watch

2) Preparation of External Standards for Steam Distillation Analysis

a) Organochlorine pesticides

α-BHC, β-BHC, γ-BHC, Heptachlor, Heptachlor epoxide, Aldrin, Dieldrin, Mirex, Methoxychlor, Chlordane, Endrin, DDT and associated compounds are each obtained in high purity from the U.S.E.P.A. Pesticide Repository. Each compound is weighed into an aluminum

TABLE 12. RECOVERY EFFICIENCIES FOR CHLORINATED PESTICIDES AND PCB's THE INITIAL STEAM DISTILLATION/EXTRACTION PROCEDURE

Compound	Recovery Range %
a-BHC	35-50
Lindane	17-30
Heptachlor	50-80
Aldrin	90-100
Heptachlor Epoxide	90-100
p,p' DDE	90-100
Dieldrin	90-100
Endrin	90-100
o,p' DDT	90-100
p,p' DDD	90-100
p,p' DDT	90-100
Mirex	90-100
Arochlor 1254	90-100
γ-Chlordane	90-100

pan and then transferred by toluene washes to a 1 ℓ volumetric flask. Individual pesticide concentrations range from 8 to 80 ng/µl.

After all materials are transferred, the volumetric flask was brought to volume by the addition of toluene. This solution was then placed into 1 ml vials and is the working solution which contains 15 organochlorine pesticides in a concentration range of 8 to 80 ng/µl. Two modifications were made to enhance recovery of chlorinated pesticides using the steam distillation apparatus; the solvent was changed from toluene to isooctane and an air condenser was used to capture non-volatile pesticides. The apparatus is illustrated in Figure 5. The procedure used for spiking and calibration is as follows:

(1) Collect 800 ml of carbon filtered water into a 1 ℓ conical flask (24/40 ST joint).

(2) Add from 2-8 µl of pesticide working solution to yield concentration range desired (2 µl = 20 - 200 ng/1, 8 µl - 100 to 1000 ng/1). The concentration used for PCB spiking was approximately 2000 ng/1 and for toxaphene 4000 ng/1.

Recovery runs are used in all cases to calibrate the gas chromatographic instrumentation. Each calibrated file is linked together to yield six separate analysis reports; 15 chlorinated pesticides, Arochlor 1016, Arochlor, 1242, Arochlor 1248, Arochlor 1254, and toxaphene.

3) Procedure

a) Rinse all steam distillation apparatus (from the top of the air condenser) with 10 ml of isooctane. Be sure to rinse the column between runs.

b) Collect this isooctane in a waste beaker and dispose of it. This should be done in a series of collections to assure that all the isooctane is removed from the apparatus.

c) Using a clean volumetric pipet, fill the columns with 5 ml isooctane. The air column can be detached when this is done and the isooctane is pipetted along the side of the column.

4) Preparing and Running the Sample

a) Agitate a 1.2 liter sample bottle before opening it to mix the sample.

b) Pour 100 to 200 ml of sample into a 1000 ml Erlenmeyer flask.

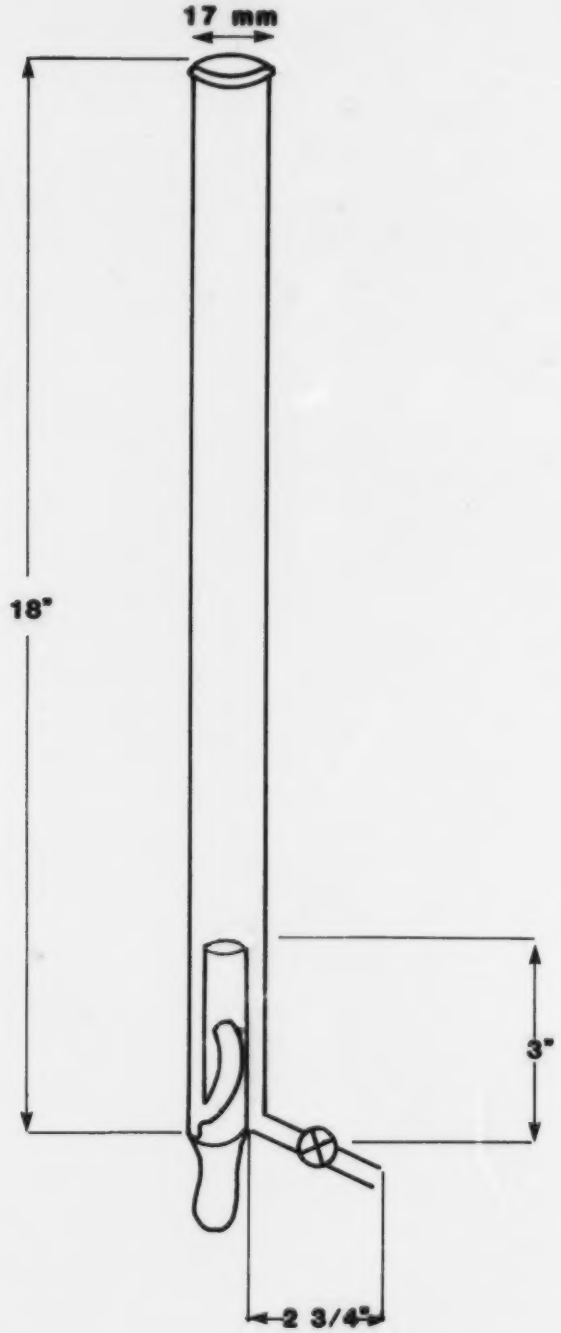

Figure 5. Steam distillation/extraction apparatus employed in halogenated pesticide and PCB determinations.

(1) Swirl the flask to rinse it thoroughly with the sample water.
(2) Pour the water into a waste pan.
(3) Transfer the tag from the 1.2 liter bottle to the flask.

c) Place a 800 ml aliquot of the sample into the 1 ℓ flask.

(1) Place two glass ebbulators into the flask at opposite ends along the bottom.
(2) Wipe all water from the outside of the flask and place it on the heating unit, so that the flask fits tightly into the condenser tube.
(3) Turn on the water so a slow steady flow circulates through the water jackets of the condensers.
(4) Turn on the heating units.
(5) Distill samples for two hours. Start to time when the sample starts to boil. At the end of the two-hour period, turn the heating unit off and let the sample cool down.

5) Documenting the Samples

a) Label four 1 ml vials with consecutive sample code numbers.

6) Removing the Samples

a) Place a clean 10 ml graduated cylinder and the corresponding numbered vials in front of the correct apparatus.

b) With a large beaker (500 ml) remove the water layer from the distillation apparatus. Drain the water so that there is still about 1 to 3 ml of water left in the column. This is to prevent any loss of isooctane.

c) Drain the remaining isooctane layer into the 10 ml cylinder. Place the cylinder back in front of the column the isooctane was taken from to avoid a mix-up of sample extract.

d) Rinse the entire apparatus down from the top with 3 ml of isooctane. (Use the same procedure as described in Sec. A-1a.) Generally, two volumes from a Pasteur pipet is roughly 3 ml, and is sufficient.

e) Drain the isooctane into the cylinder with the first extract.

f) Using a clean Pasteur pipet, remove the water layer from the cylinder and place it in a waste beaker. Make sure no isooctane is being disposed of.

g) Using fresh isooctane and a new pipet, bring the level of isooctane in the cylinder up to 8 ml. Be sure all water is removed before this is done.

h) Transfer the 8 ml in the cylinder to the corresponding four vials and seal the tops. If any seals are damaged or the septa bulge at the top, the vial must be resealed.

7) Cleaning Steam Distillation Glassware

a) Rinse the columns with 10 ml of isooctane as previously described.

b) Remove the flasks from the condensers, being careful not to break the glass boil easers and empty out the water.

c) Remove any writing on the flask.

d) Rinse the flasks and glass boil easers thoroughly with tap water and store.

e) Wash glass cylinders in hot, soapy water; rinse in tap water, distilled water and acetone, then bake for no less than one hour in the oven at 250°C.

f) All pipets except volumetric pipets are to be disposed of.

8) Procedure Evaluation

The recoveries obtained by this modified procedure are presented in Table 13, along with the recovery variations to be expected. The minimum reportable concentrations are presented in Table 14. Typical chromatograms for pesticides, Arochlor 1016 and toxaphene are shown in Figures 6-8. Quality assurance results are presented in Table 15.

F. DETERMINATION OF CHLOROPHENOLS

1. Procedures

A procedure similar to Chau and Coburn (1974) was used. The basis of the method is extraction, generation of the phenolate anion, acylation of the phenol and extraction of the acylated phenol into a non-polar solvent. The exact procedure is as follows:

a. A 1.2 liter sample is collected in a narrow mouth glass bottle with a Teflon screw top (cleaning procedure is the same as described in Sec. 2-A.2. for PCB, chlorinated pesticide and toxaphene analysis).

b. 10 mg/l of free chlorine is added to each sample (as measured by DPD method for free chlorine).

c. The chlorinated samples are stored at 20°C (in the dark) for seven days.

TABLE 13. RECOVERY INFORMATION FOR SECOND DISTILLATION/EXTRACTION PROCEDURE

Compound	Standard Concentration µg/l	Mean* Recovery %	Standard Deviation µg/l
BHC-α	79.8	97.1	± .26
BHC-γ	84.8	85.1	± .36
BHC-β	106.2	24.7	± .40
Heptachlor	86.2	18.1	± .13
Aldrin	73.5	95.9	± .79
Heptachlor epoxide	79.1	100.8	± .35
γ-Chlordane	77.5	105.8	± .54
P,P' DDE	140.0	102.2	± .66
Dieldrin	164.0	103.8	± .48
Endrin	180.0	79.0	± .90
o,p' DDT	713.4	111.1	± 3.07
p,p' DDD	200.0	95.0	± .86
p,p' DDT	698.3	113.0	± 3.63
Mirex	235.1	93.4	± 2.63
Methyoxychlor	800.5	108.0	±19.77
Arochlor	1917	89.7	±32.59
Arochlor	2152	99.4	±39.81
Arochlor	2074	98.1	±17.21
Arochlor	2206	85.0	±11.47
Toxaphene	4000	65.8	±10.40

*n = 4

TABLE 14. MINIMUM REPORTABLE CONCENTRATIONS FOR SECOND STEAM DISTILLATION/EXTRACTION PROCEDURE

Compound	Minium Reportable Concentration µg/l
BHC - α	10
BHC - γ	10
BHC - β	10
Heptachlor	10
Aldrin	10
Heptachlor epoxide	10
γ - Chlordane	10
p,p - DDE	10
Dieldrin	10
Endrin	10
o,p' - DDT	40
p,p' - DDD	20
p,p' - DDT	40
Mirex	20
Methoxychlor	80
Arochlor 1016	60
Arochlor 1242	60
Arochlor 1248	60
Arochlor 1254	60
Toxpahene	600

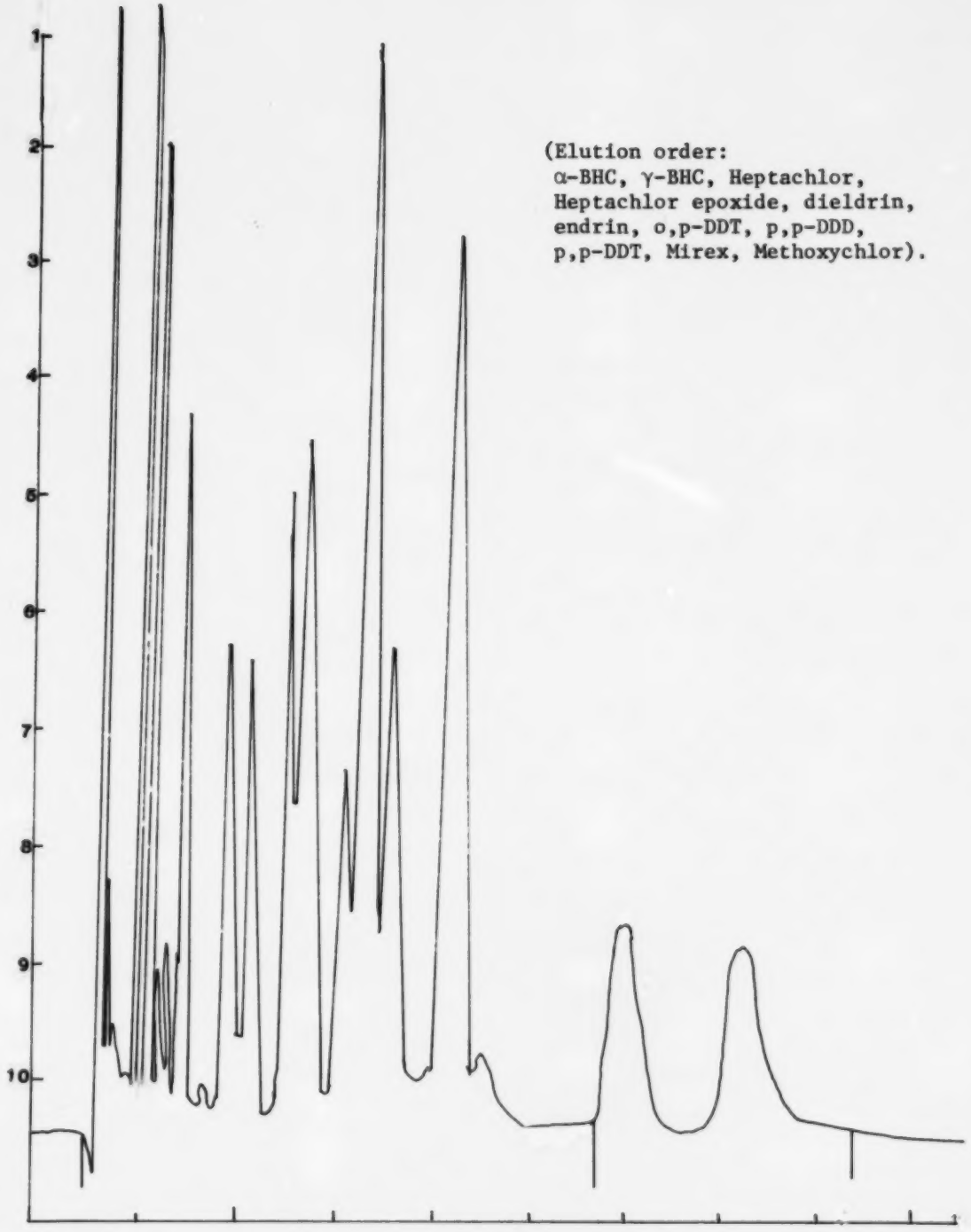

Figure 6. Typical pesticide chromatogram.

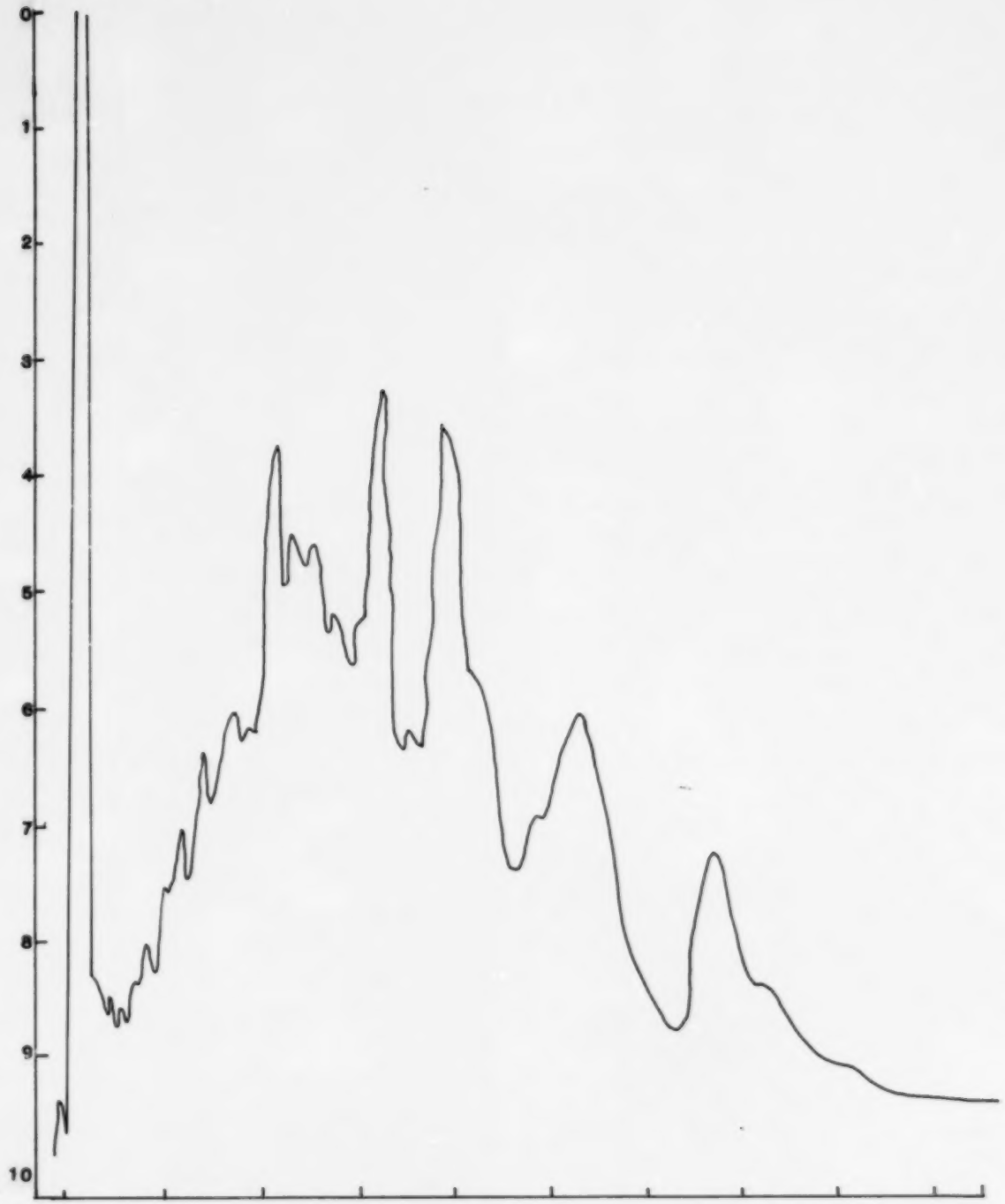

Figure 8. Typical chromatogram for toxaphene.

TABLE 15. EPA QUALITY ASSURANCE (PCB-476) SAMPLE FOR PCB ANALYZED BY MODIFIED STEAM DISTILLATION PROCEDURE AND PACKED COLUMN GAS CHROMATOGRAPHY

PCB Type	Results mg/l Sample 1 Found	Sample 1 True	Sample 2 Found	Sample 2 True	Sample 3 Found	Sample 3 True
1016			0.71±0.04	0.65	0.33±0.02	0.26
1254	1.07±0.04	0.96			0.57±0.02	0.58

d. Before initial extraction, the samples are agitated to resuspend any settled material.

e. One hundred ml of sample is removed leaving 1100 ml remaining for analysis.

f. The sample is acidified to a pH 2.0 with concentrated H_2SO_4.

g. The acidified sample (1100 ml) is extracted with 3 x 50 ml of trimethyl pentane. Extracts are transferred to a 250 ml separatory funnel.

h. The chlorinated phenols are partitioned into a basic solution (3 x 15 ml washes of 0.1 N NaOH).

i. The basic aqueous solution (45 ml is transferred to a 60 ml capacity culture tube with a Teflon-lined screw top (10 mm x 200 mm).

j. One ml of acylation reagent (2/1 (V/V) pyridine acetic anhydride together with 5 ml of trimethyl pentane is added to the basic solution.

k. The sample is agitated for three minutes on a wrist action shaker.

l. The phases are allowed to separate and the upper (trimethyl pentane) phase containing the acylated phenols is removed and subjected to a gas chromatographic procedure.

2. Gas Chromatography Procedure for the Determination of Acylated, Chlorophenols

a. Conditions

1) Injection Temperature = 20°C

2) Oven Temperature = 200°C isothermal

3) Detector Temperature = 300°C

4) Detector Type N^{63} (8 mci) 50 V.D.C. pulsed mode

5) Carrier gas H_2 at 60 cm/sec approximately 1.7 ml/min.

6) Makeup gases 20 ml/min. at detector base N_2 + 20 ml/,min. at column end N_2.

7) Injection Volume = 3 µl

b. Calibration and Quantitation

The gas chromatographic data system was calibrated by an external

standard method. This procedure uses a spiked recovery extract as a standard and automatically corrects for recovery through the extraction procedure. Figure 9 illustrates a typical gas chromatograph for the five chlorinated phenols used as external standards.

G. PROCEDURE FOR PURGE AND TRAP ANALYSIS OF VOLATILE ORGANIC COMPOUNDS USING GC/MS DETECTOR

A Tekmar LSC-1 apparatus was used, with a 50 ml sparger in place of the normal 5 ml sparger as the sample presentation device. The purge conditions were as follows:

purge gas flow 50 ml/min He
carrier gas flow 20 ml/min He
purge time 20 min.
desorb time 5 min.
desorb temperature 180°C
trap material 2/3 tenax GC (60/80) + 1/3 silica gel type 15
sample size 50 ml

The desorbed sample was vented to a Finnigan 3100 GC/MS using a 20% SP2100 + 0.1% CW 15M 10' x 2 mm stainless steel chromatographic column. GC and MS conditions were as follows:

initial temperature 40°C for 5 min
program rate 8°C/min
final temperature 150°C
injector temperature 100°C
carrier flow 20 ml/min He
separator and transfer line temperature 250/250°C
scan range 40-275 AMV

Identification of compounds was done by interpretation of oscillographic recording obtained at the peak of each eluting component and quantitation by comparison of peak heights of identified compound versus standards (prepared in the same manner) using total ion abundance response chromatograms.

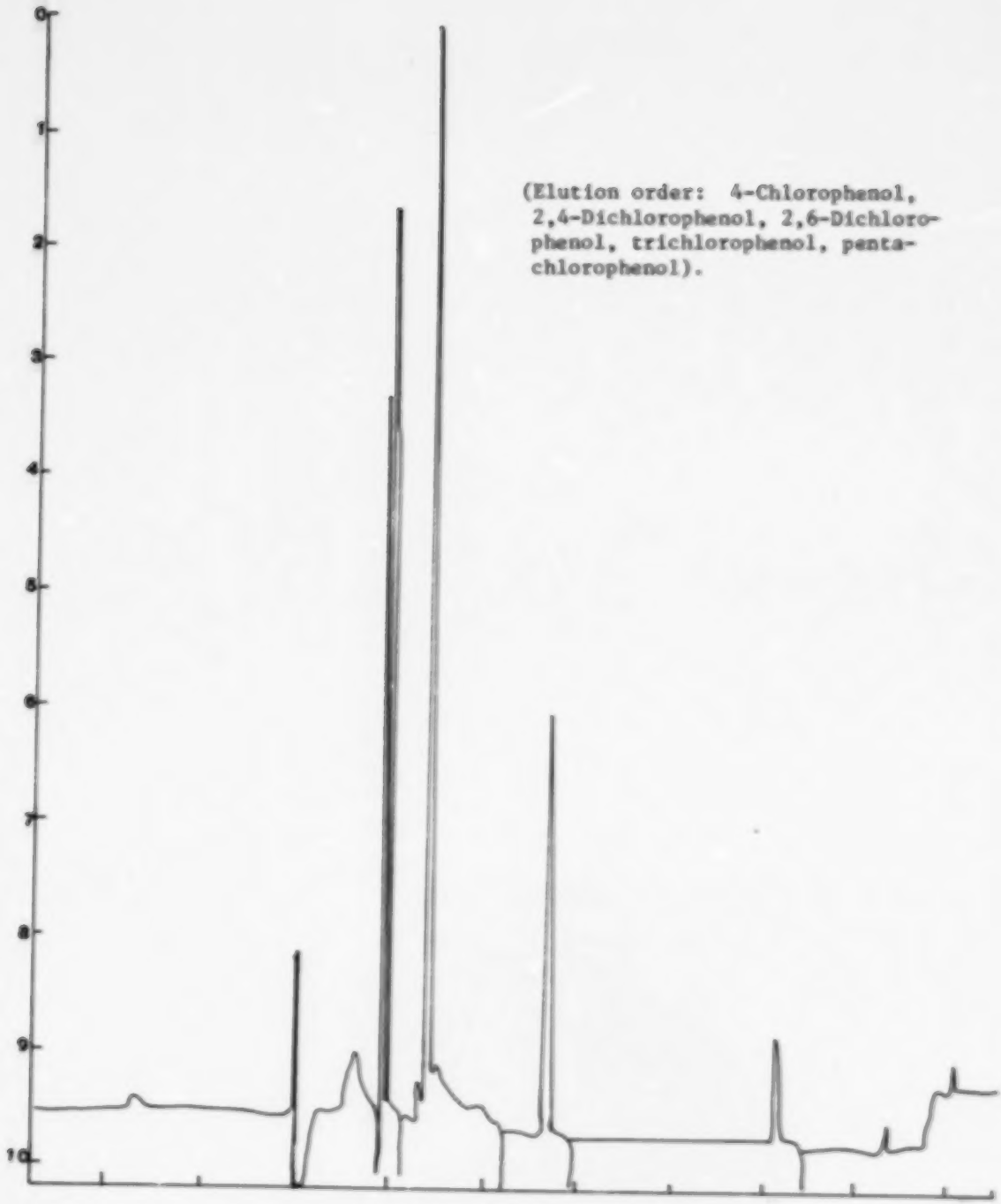

Figure 9. Typical chromatogram for halogenated phenols.

SECTION 5

RESULTS AND DISCUSSION

The results of this study may be divided into two parts. The first deals with the halocarbons found in the water. The second deals with those (mainly halomethanes) formed during chlorination.

PART I: HALOCARBONS PRESENT IN WATER SUPPLY

A. PRELIMINARY MONITORING FOR HALOCARBONS

Volatile halogenated hydrocarbons were determined in the watershed at a number of sampling stations. These compounds were isolated by a purge and trap procedure and were separated and determined by use of a Finnigan 3100-D GC/MS using a packed column. The results of these analyses are presented in Table 16.

The results of quantitative analysis revealed that during summer samplings, chloroform and dichlorobromomethane were the predominant volatile halogenated hydrocarbons observed. This seemed reasonable because the two materials are the result of chlorination practices, and that over 100 sewage and industrial discharges are located on the watershed. On the other hand, the results of winter samplings (all under ice cover) showed that methylene chloride was the predominant halomethane. This observation agreed with the fact that at very low temperatures (<4°C) haloform formation is greatly reduced (kinetically controlled reaction) and that under ice cover evaporation or air stripping was minimal. Thus, direct industrial discharge is the probable source of methylene chloride, and its impact on the water quality of the Passaic River is accentuated during ice cover.

B. WATERSHED SURVEY AND MASS BALANCE FOR PCB AND HALOCARBONS

Several sets of samples were obtained on 7/15-16/76, 7/21/76, 8/26/76 and 1/29-30/76. The volatile halogenated organics were determined by purge and trap followed by packed column GC employing an electron capture detector. Pesticides and PCB's were determined by steam distillation/solvent extraction followed by GC employing a packed column. These procedures are detailed in Section 4.

The concentration and loadings of the volatile halogenated hydrocarbons and PCB's are presented in Tables 17 and 18, respectively. The concentra-

TABLE 16. PRELIMINARY VOLATILE HALOCARBON SURVEY

Sampling Station	Sampling Date	Component Concentrations (ppb) CH_2Cl_2	$CHCl_3$	CCl_3CH_3	$CHCl_2Br$	$CHClCCl_2$	$CHClBr_{2+}CCl_2CCl_2$	$CHCl_2CHCl_2$
Fritzche D.O.	8/26/76			2.0				
PVWTC Raw Water	8/20/76		0.2	1.9				
110	7/15/76	1.0	1.8	2.4				
Berkley Hts., STP Contractor #1	7/15/76	2.4	2.8	3.4	1.2		1.2	
PVWTC Delivered* Water	8/20/76	0.2	10-100	3.0	15.2		2.2	
PVWTC Water after BPC †	8/20/76	1.0	10-100	6.0	10-100		3.2	
Livingston STP	7/15/76	3.8	10-100	10.6	4.6		2.2	
Bell Telephone	8/26/76	>1.0ppm				>1.0ppm		
251-I Whippany Paper Board Co.	7/21/76	0.5	1.6	2.6				
Ramapo Coll. STP	7/21/76	1.5	11.5	2.0	5.2			
180	7/21/76	0.5	2.4	2.6	1.5			
Airtron Litton Co.	8/26/76	0.8		2.0	0.5			
Curtis Wright Co.	8/26/76	2.2	7.2	0.6		10.0		
Norda Chemical	8/26/76	0.3	0.2	0.8				
ITT Ranier Co.	8/26/76	0.4	0.2	0.1				
251-I Whippany Paper Board Co.	8/26/76	3.6	4.0	10-100		2.2	6.0	1.4

(Continued)

TABLE 16 (Continued)

Sampling Station	Sampling Date	Component Concentrations (ppb) CH_2Cl_2	$CHCl_3$	CCl_3CH_3	$CHCl_2Br$	$CHClCCl_2$	$CHClBr_2$	CCl_2CCl_2	$CHCl_2CHCl_2$
670	8/21/76	1.8	0.2	2.6					
210	7/21	1.7	6.8	5.8	0.5			0.1	
160	7/15/76	2.8	2.5	1.8	0.3				
410	7/21/76	1.8	1.4	0.8	0.4				
Crooked Brook	7/21/76	4.0	3.4	0.9					
321-B-3	7/21/76	6.4	3.2	0.4	4.4				
Butler Bloomingdale STP	7/21/76	2.8	4.8	0.2					
250	7/16/76	1.6	3.2	0.6					
510	7/21/76	No detectable components							
Nu Car Carriers Mahwah, N.J.	7/21/76	1.4	10-100	1.5	10-100		5.0		
710	7/21/76	11.0	5.2	1.4					
Village of Suffern STP	7/21/76	3.8	7.4	3.4				0.4	1.0
Ciba Chemical Summit, N.J.	7/15/76	10-100	10-100	2.4					
321-B-3	7/16/76	20.0	13.2	4.2	1.6			1.4	
Sharky's Old Dump adj. 210	7/17/76	6.0	4.4	2.4	0.6			0.5	
260	7/21/76	13.0	6.6	5.2	0.6			0.4	

(Continued)

TABLE 16 (Continued)

Sampling Station	Sampling Date	Component Concentrations (ppb) CH_2Cl_2	$CHCl_3$	CCl_3CH_3	$CHCl_2Br$	$CHClCCl_2$	$CHClBr_2$	CCl_2CCl_2	$CHCl_2CHCl_2$
Wanaque STP	7/21/76	1.2	7.0	2.4	3.2			10-100	
290	7/21/76	1.4	4.2	1.6	0.5				
Caldwell STP	7/15/76	0.8	4.6	2.4	0.2				
180	7/15/76	6.0	4.8	2.2	0.1			0.1	
350	7/21/76	2.2	5.2	2.5	0.2				
Berkley Hts. Chem. Co.	7/15/76	11.8	7.8	1.2	0.4				

* Passaic Valley Water Treatment Commission Delivered Water from Little Ferry, N. J. Plant

† PVWTC plant water after break point chlorination

≠ Standard not available estimated from $CHCl_2Br$ calibration curve

TABLE 17. CONCENTRATIONS AND LOADING OF VOLATILE HALOGENATED HYDROCARBONS (12/29-30/76)

Station	Flow MGD	CH_2Cl_2 ppb	CH_2Cl_2 kg/day	$CHCl_3$ ppb	$CHCl_3$ kg/day	CH_3CCl_3 ppb	CH_3CCl_3 kg/day	$CHCl_2Br$ ppb	$CHCl_2Br$ kg/day	$CHClBr_2$ ppb	$CHClBr_2$ kg/day	ODCB ppb	ODCB kg/day	1,2,4-TCB ppb	1,2,4-TCB kg/day
725	59.5	44	9.91	0.4	0.09	18.4	4.14	0.1	0.02	---	---	---	---	---	---
705	67.0	900	228.3	15.9	4.03	14	3.55	0.1	0.03	---	---	---	---	---	---
530	11.6	96	4.22	---	---	---	---	---	---	---	---	---	---	---	---
450	8.78	75	2.49	0.5	0.02	---	---	---	---	---	---	---	---	---	---
650	92.5	560	196.1	5	1.75	26.8	9.38	---	---	1.2	0.42	---	---	---	---
330	16.0	30	1.82	1.5	0.09	11.6	0.70	0.5	0.03	---	---	---	---	---	---
280	16.4	1	0.06	2.8	0.17	18.4	1.14	1.4	0.09	---	---	0.4	0.03	0.4	0.03
180	N/A	---	---	0.25	---	30	---	0.1	---	---	---	0.7	---	2.4	---
165	21.0	5	0.40	---	---	---	---	---	---	---	---	---	---	---	---
100	225.0	88	74.95	3.6	3.07	37.6	32.02	0.4	0.34	0.5	0.43	---	---	---	---
D.W.	49.0	230	42.66	2	0.37	---	---	5.5	1.02	---	---	---	---	---	---

TABLE 18. CONCENTRATION AND LOADING OF PCB'S

Sampling Station	Date	PCB (as 1242) µg/l	Flow MDG	Loading Kg/day
Finished water	12/30/76	1.75	49.0	0.325
After filtration	12/30/76	2.95	49.0	
After BPC*	12/30/76	2.75	49.0	
100	7/16/76	1.15		
100	7/15/76	7.70		
100†	12/30/76	17.85	225.0	15.2
110	7/16/76	2.38		
140	7/16/76	1.40		
165	12/30/76	1.20	21.0	0.095
180	12/29/76	2.52		
210	7/16/76	1.90		
220	7/16/76	0.80		
250 WF‡	7/16/76	2.65	16.8	0.169
260	7/16/76	2.56		
280	12/29/76	0.55	16.4	0.034
321-B-3	7/16/76	0.15		
321-B-3	7/21/76	0.20		
330	12/29/76	3.45	16.0	0.209
410	7/16/76	0.95		
450	12/29/76	2.76	8.78	0.092
530	12/30/76	0.50	11.6	0.022
610	7/16/76	1.58		
650	7/15/76	1.20		
650 WF	7/16/76	1.10		
705	12/29/76	13.0	67.0	3.30
725	12/29/76	2.10	59.5	0.473

(Continued)

TABLE 18 (Continued)

Treatment Plants	Date	PCB (as 1242) µg/l	Flow MGD	Loading kg/day
Totowa West End STP	7/16/76	198.0	0.77	0.577
Butler Bloomington STP	7/21/76	0.77	1.6	0.005
Industrial Plants				
Whippany Paper Board (251-1)	7/21/76	0.78	4.3	0.013
Berkeley Hts. Chemical Co.	7/15/76	3.31	1.6	0.020

* Breakpoint chlorination

† Only 49 mgd was processed by the PVWC on that date = 3.31 kg

‡ Wet flow

tions of pesticides are shown in Table 19. As these were winter samples, methylene chloride was the dominant volatile halocarbon, followed by methyl chloroform. The haloforms were present but not at levels comparable to these. The dominant halogenated pesticide present was α-BHC, but other steam distillable halogenated materials were present as indicated by the number of unidentified peaks.

Stream loadings of both PCB's and VOA's were calculated where flow data were available. These may be summarized for the PCB's in the stream samples taken 1/29-30/76 as follows:

100 series	0.95 kg/day
200 series	0.035 kg/day
300 series	0.209 kg/day
400 series	0.092 kg/day
500 series	0.022 kg/day
700 series	0.473 kg/day
Total Loading	0.925 kg/day

The calculated loading in the Passaic River at the plant intake was 15.2 kg/day. Thus, stream samples account for only 6.1% of PCB's at the treatment plant intake. This would indicate an additional input of approximately 14.3 kg/day in that stretch of river after the confluence of the Ramapo and Pompton Rivers to the intake of the PVWC plant at Little Falls. This sparked an investigation of the Totowa West End sewage treatment facility which exhibited a one-time concentration of 198 µg/l of Arochlor 1242. The STP outfall is located one-half mile upstream of the PVWC intake. A resampling of the effluent indicated the presence of 5 ppb of Arochlor 1242 (this was confirmed by EPA Region II Laboratory). The sewage authority determined that a capacitor manufacturer discharging into their system was the cause. An enforcement of good housekeeping practices at the manufacturing facility resulted in no detectable PCB at the PVWC intake on a number of subsequent samplings.

Sum of halomethane loadings including methylene chloride in stream samples for 12/29-30/76 sampling:

100 series	0.40 kg/day	600 series	198.0 kg/day
200 series	0.32 kg/day	100 series	0.4 kg/day
300 series	1.94 kg/day	Total	198.4 kg/day
400 series	2.50 kg/day		
500 series	4.22 kg/day		
700 series	233.00 kg/day		
Total	242.38 kg/day		

$$\frac{\text{Intake}}{100 + 600 \text{ series}} \times 100\% = \frac{78.8}{198.4} = 39.72\%$$

This is a rough indication that a large part of halogenated methanes do reach the intake of the PVWC plant when ice cover is present, although they are largely methylene chloride.

TABLE 19. TYPE AND CONCENTRATION OF HALOGENATED PESTICIDES

Station	Date	# of ECD Peaks	Pesticides* Identified	Concentration PPT†
Finished Water‡	7/16/76	4	α-BHC	1
Finished Water	8/25/76	2	-----	---
Finished Water	8/23/76	1	-----	---
106-B	7/21/76	2	-----	---
130	7/16/76	2	-----	---
160	7/15/76	0	-----	---
210	7/16/76	1	-----	---
Drainage adjacent to 210	7/16/76	2	α-BHC B-BHD	14 14
250	7/21/76	1	-----	---
260	7/21/76	2	-----	---
280	7/16/76	3	-----	---
290	7/21/76	2	α BHC B-BHC	20 10
310	7/15/76	8	α-BHC	7.5
310	7/16/76	4	α-BHC	5.5
321-B-3	7/15/76	1	-----	---
510	7/15/76	3	α-BHC B-BHC	13 13
670	7/21/76	0	-----	---
710	7/15/76	5	-----	---
710	7/21/76	1	-----	---
725	7/21/76	5	-----	---
Sewage Treatment Facilities				
Butler Bloomingdale STP	7/16/76	7	-----	---
Par-Troy STP	7/21/76	6	α-BHC	6.5
Ramapo College STP	7/21/76	0	-----	---
Wayne Sheffield STP	7/16/76	7	α-BHC	18
Morristown STP	7/15/76	4	α-BHC	100

(Continued)

TABLE 19 (Continued)

Station	Date	# of ECD Peaks	Pesticides* Identified	Concentration PPT†
Caldwell STP	7/15/76	3	-BHC	18
Wayne Municipal STP	7/16/76	5	-----	---
Berkeley Hts. STP	7/16/76	4	-BHC	6
Wanaque STP	7/16/76	5	-BHC	44
Passaic Township STP	7/15/76	5	-BHC	12
Livingston STP	7/15/76	1	-----	---
Hanover STP	7/16/76	6	-BHC	400
Totowa West End STP	7/16/76	5+PCBs	Heptachlor epoxide	350
Madison Chatham STP	7/16/76	3	-BHC	13
Industrial Plant Effluents				
Whippany Paper	7/21/76	7	-----	---
Board Co. (251-I)	7/15/76	2	-----	---
ITT Ranior Div.	8/26/76	1	-----	---
NU Car Carries	7/16/76	2	-----	---
Ciba Chemical Co.	7/16/76	2	-----	---
Norda Chem. Co.	8/26/76	1	-----	---
Fritache D.O. & Co.	7/16/76	5	-BHC	1
	8/26/76	0	-----	---
Bell Telephone Co.				
Manufac. Plant	8/26/76	1	-----	---

* Tentatively identified on 1.95% SP-2250 plus 1.5% SP-2401

† Parts per trillion

⊕ PVWC delivered water

C. MONITORING VARIATION OF HALOGENATED MATERIALS IN PVWC TREATMENT PLANT—RAW AND FINISHED WATERS

Because most of our sampling was conducted on a grab basis, it was necessary to obtain some indication of the variation in concentration of all monitored chlorinated compounds in both raw and finished waters at the Passaic Valley Water Commission treatment facility. Plant personnel obtained all samples for this survey. Sample containers were solvent washed and baked at 250°C before use. Sampling was conducted every eight hours for a period of five days, and all samples for volatile halogenated hydrocarbon analysis were fixed with $Na_2S_2O_3$ in the field.

The n-pentane extraction procedure was used for the isolation of volatile halogenated hydrocarbons while the exhaustive steam distillation/extraction procedure was employed to obtain a suitable extract for high boiling halogenated hydrocarbons. A set of five daily samples were also collected from the Totowa West End S.T.P. for PCB/pesticide analysis, and were treated by the procedure mentioned above.

The results of this study for the haloforms are presented in Figures 10-12 and for carbontetrachloride and tetrachloroethylene in Figures 13 and 14. As would be expected, the finished water contained larger amounts of the haloforms than did the raw water, with dichlorobromomethane being the major constituent. Concentrations were variable ranging from 34-90 µg/1.

These can be contrasted with carbontetrachloride and tetrachloroethylene which are "not" formed during chlorination. These show marked variation in both raw and finished waters. These results suggest that there is an upstream discharge of these two materials. In the case of CCl_4 the discharge is on a periodic basis and the present plant treatment processes attenuate the raw water concentration only to a small degree. The finished water concentration for CCl_4 is in excess of 7 ppb in one instance. The source of these two halogenated materials is not yet known; but future stream sampling may identify a source.

Higher boiling chlorinated hydrocarbons were not detected, either in the raw or finished water during this monitoring survey, although they had been detected previously. Recall that the minimum detectability of PCB's (as Arochlor 1242) is 0.05 ppb and approximately 10 to 20 parts per trillion for most organochlorine pesticides.

D. CHLORINATED PHENOLS

Samples of water were collected at various sampling stations and were analyzed for halogenated phenols according to the procedure noted in Section 4. The results are presented in Table 20. All stations sampled showed some chlorinated phenols, especially the upstream Passaic River samples. As would be expected, the chlorinated finished water contained more chlorinated phenols than the immediate raw waters, but none contained the variety or quantity of the phenols found in the upstream Passaic.

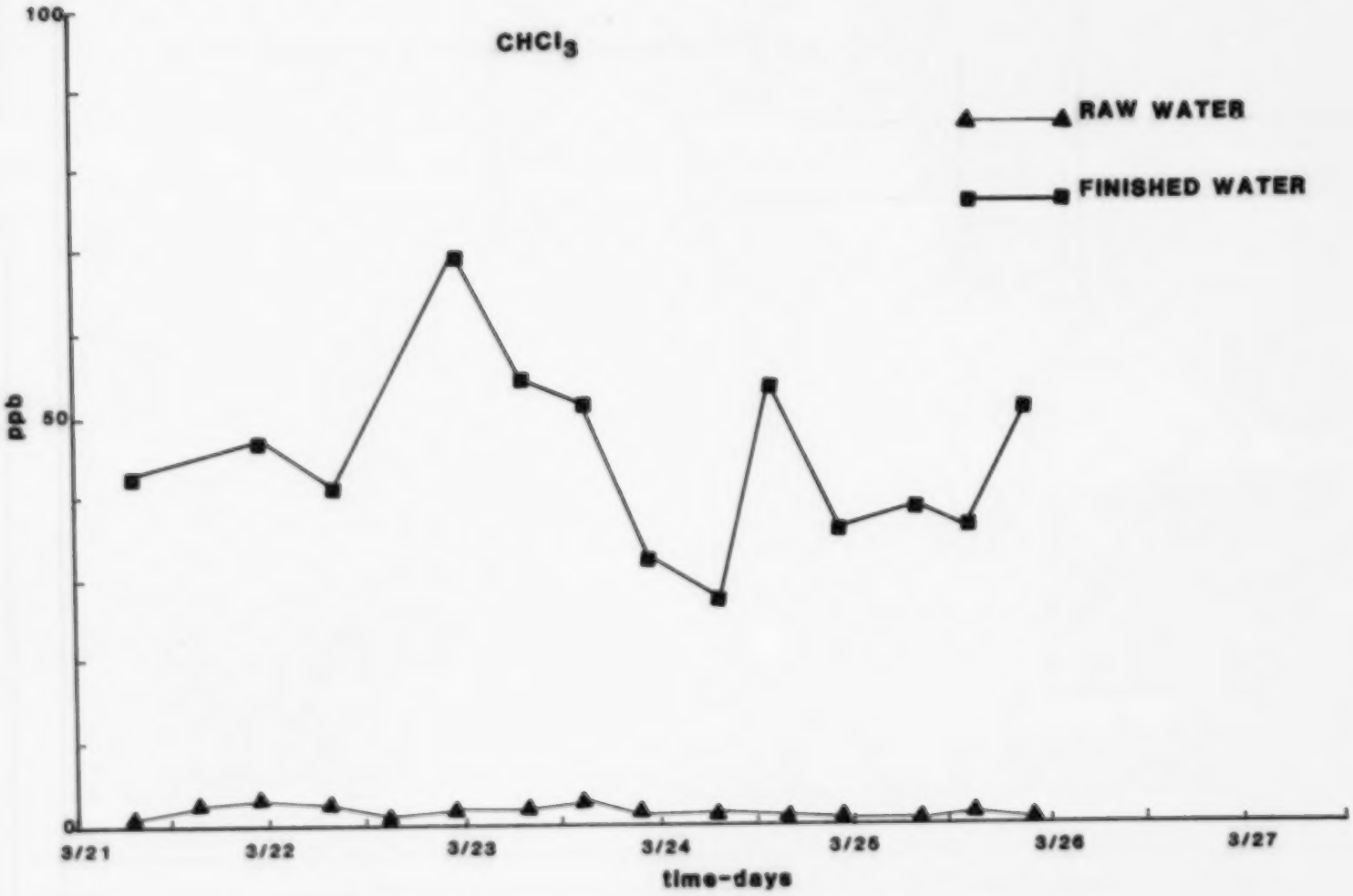

Figure 10. Variation of chloroform concentrations with time at the PVWC treatment plant.

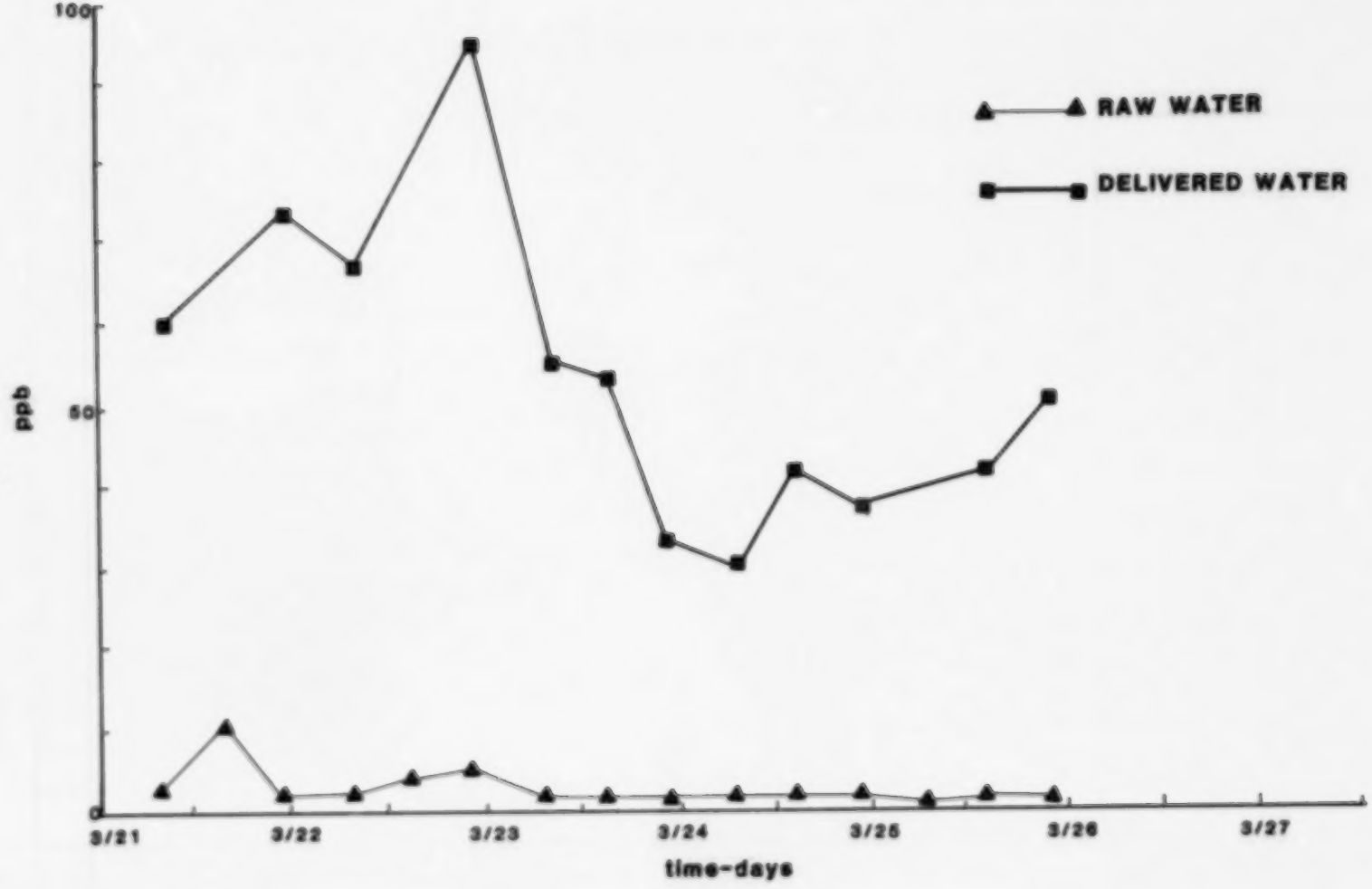

Figure 11. Variation of dichlorobromomethane concentrations with time at the PVWC treatment plant.

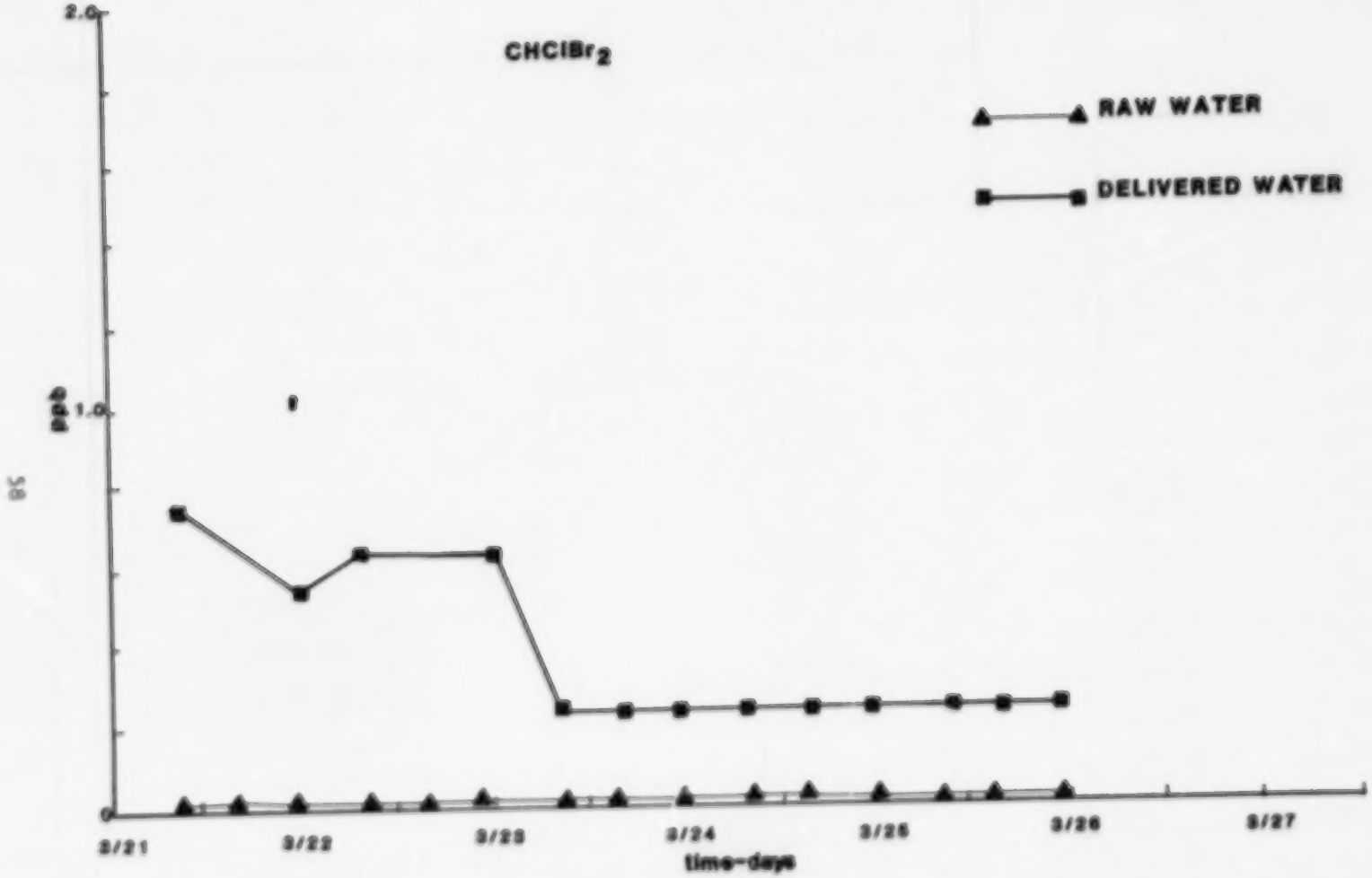

Figure 12. Variation of dibromochloromethane concentrations at the PVWC treatment plant.

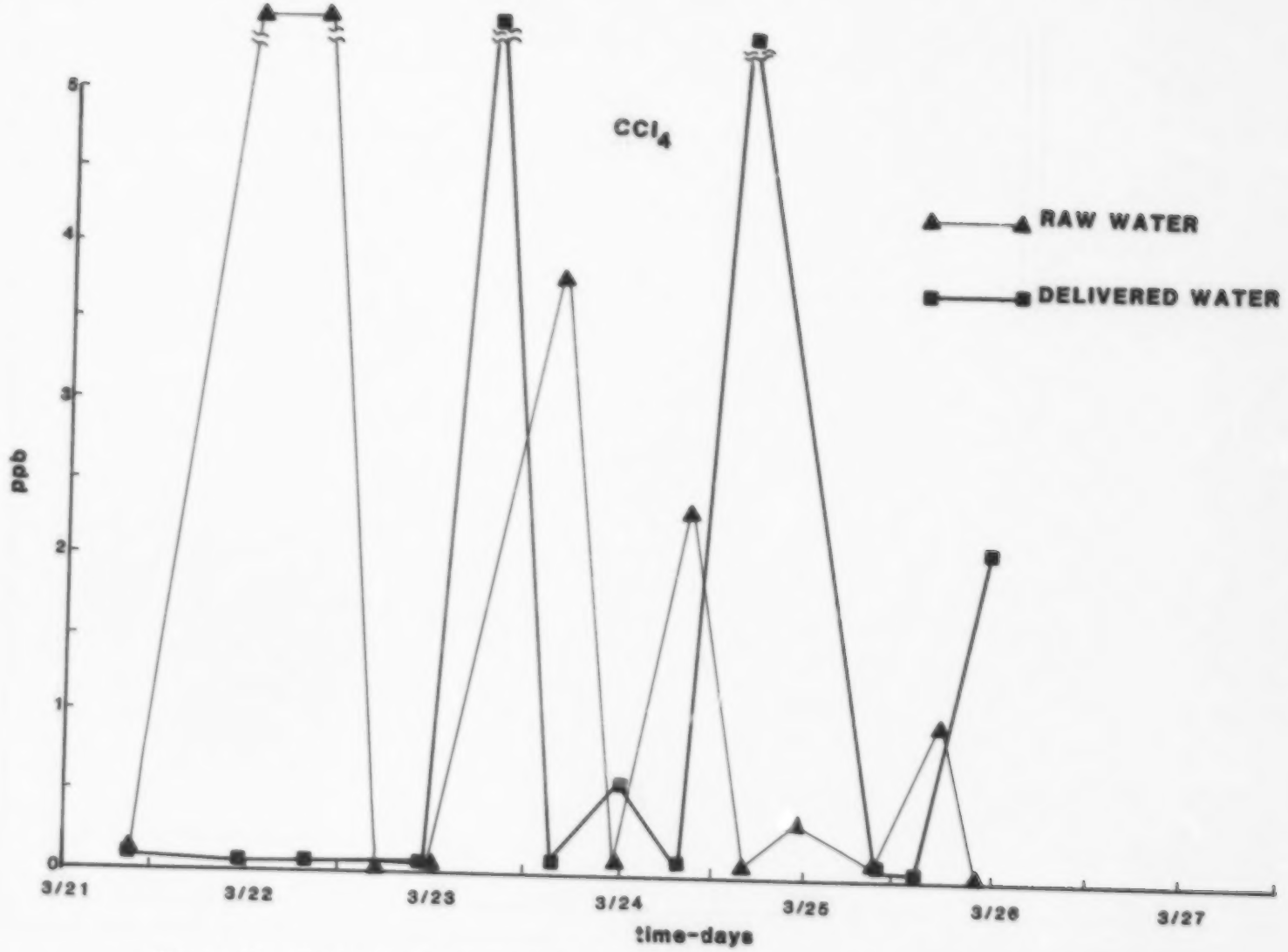

Figure 13. Variation of carbontetrachloride concentrations at the PVWC treatment plant.

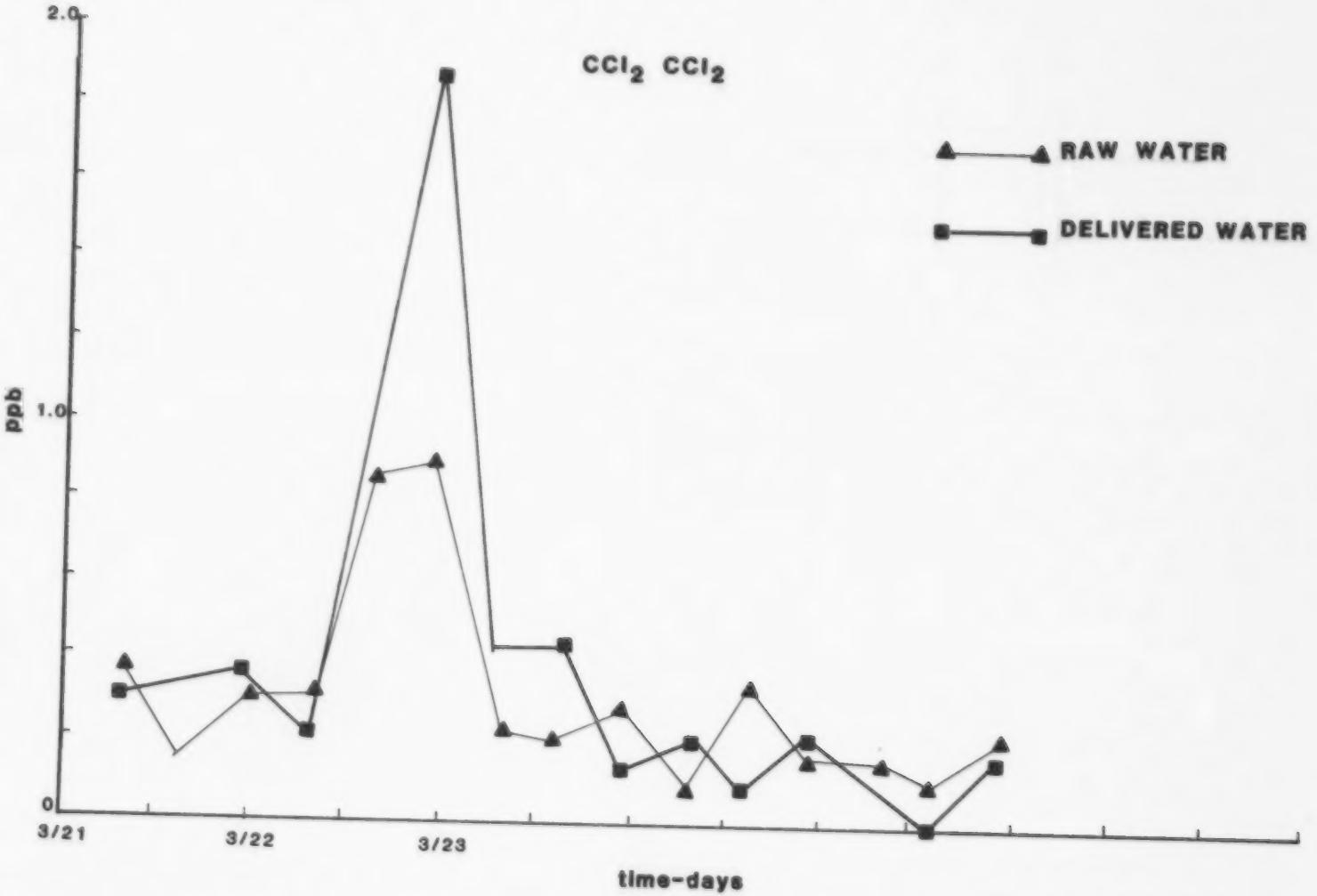

Figure 14. Variation of tetrachloroethylene concentrations in the PVWC treatment plant.

TABLE 20. RESULTS OF CHLOROPHENOL STUDY FOR 1/6/78
CONCENTRATION IN ng/1 (^{N}=3)

	Chlorophenol*				
Station No.	1	2	3	4	5
180	----	----	10±7	80±7	401±15
610	20±7	----	4±0	48±1	231±6
440	----	----	23±5	30±0	161±6
Finished Water (Passaic)	122±5	----	3±1	----	-----
230	----	----	22±1	----	-----
725	10±0	----	5±2	----	-----
100	----	----	23±1	----	-----
Finished Water (Mixed)	14±1	----	6±0	----	-----
Finished Water (Wanaque)	----	----	17±1	----	-----
310	----	----	6±0	----	-----
810	79±10	22±10	15±2	38±2	-----
530	----	49±7	12±0	----	-----
Wanaque Resevoir	----	----	13±2	----	-----

1 = 2, 6-dichlorophenol

2 = 2, 4=dichlorophenol

3 = Trichlorophenol

4 = Tetrachlorophenol

5 = Pentachlorophenol

PART II: HALOCARBONS FORMED THROUGH CHLORINATION

A. TRIHALOMETHANE FORMATION POTENTIAL OF STREAM SAMPLES

A number of stream samples were collected and analyzed for their volatile halogenated hydrocarbon constituents. The procedure employed was solvent extraction followed by packed column GC as detailed in Section 4. The results of this study are presented in Table 21. Duplicate samples were treated with 14.2 ppm of chlorine (as NaOCl solution) and allowed to react for three hours to mimic PVWC plant conditions. The production of total trihalomethane (the sum of $CHCl_3$, $CHCl_2Br$, $CHClBr_2$ and $CHBr_3$ for these samples) was determined and corrected for initial haloforms if present. These data are presented in Table 22. The range of trihalomethane formation potential (THMFP) was from 20.3 to 282 ppb, with most results falling near 100 ppb.

Comparing the results of the finished Passaic River water for 5/13/77 against chlorinated station 100 (raw water) for the same date, there is a reduction of 22% of total trihalomethane formation using standard plant treatment practices. The largest THMFP values were obtained on the upper Passaic River. These high values are probably due to the large volume of treated sewage discharged to that stretch of the river. The reduction in the trihalomethane formation potential through conventional treatment processes is due to the removal of the trihalomethane precursors (mainly particulate organics) by flocculation and filtration.

B. COMPARISON OF TWO WATER SOURCES FOR TOTAL TRIHALOMETHANE FORMATION POTENTIAL

The Passaic Valley Water Commission used both the Passaic River and the Wanaque Reservoir as raw water supplies. Both instantaneous (quenched) and terminal trihalomethane analyses were performed for the two finished waters. The Wanaque Reservoir source water is initially chlorinated at the reservoir without any additional treatment. The chlorinated source water is then piped to the Passaic Valley Water Treatment Plant in Little Falls, New Jersey, where it undergoes filtration. The chlorinated finished water then enters the distribution system and mixes with Passaic River treated water. Since the locations of these stations are mainly within the plant/distribution system, the previously employed sample station identification numbers are not applicable. These may be identified as follows:

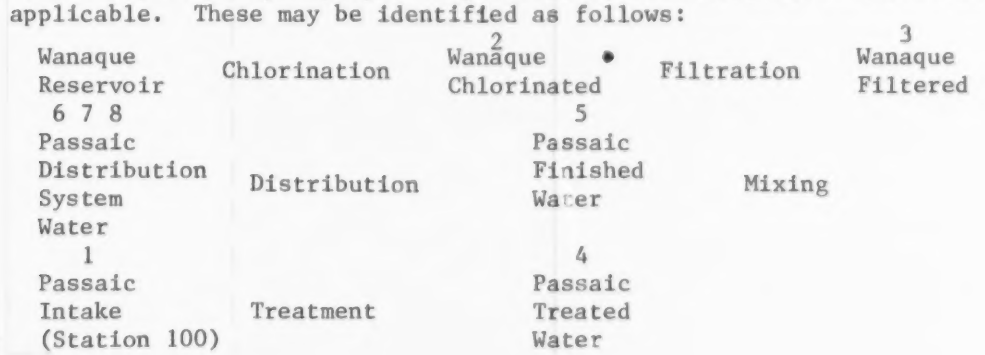

TABLE 21. RESULTS OF STREAM SAMPLES FOR VOLATILE HALOGENATED HYDROCARBONS

Sampling Date and Station	$CHCl_3$	CCl_4	$CHCl_2Br$	$CHClBr_2$ (µg/ℓ)	CCl_2CCl_2	$CHBr_3$	$CHCl_2CHCl_2$	UK*
5/4/77 - 100	1.48	0.03	0.69	0.02	0.49	----	----	3
5/4/77 - 100	1.27	0.04	1.-0	----	0.46	----	----	3
5/4/77 - 110	1.53	0.33	0.33	----	0.30	----	----	2
5/4/77 - 115	25.34	0.02	73.60	0.04	24.63	----	----	3
5/4/77 - 410	0.74	0.02	1.47	----	0.68	----	----	4
5/4/77 - 510	0.53	0.03	0.31	----	0.10	----	0.03	4
5/4/77 - 540	0.88	0.07	0.69	0.01	0.89	----	----	4
5/4/77 - 610	0.48	0.03	0.26	----	0.27	----	----	2
5/4/77 - 630	0.39	0.02	0.27	----	0.28	----	----	2
5/4/77 - 660	0.41	0.02	0.19	----	0.20	----	----	1
5/4/77 - 670	1.60	0.41	3.25	----	----	0.04	0.15	7
5/4/77 - 710	0.42	0.03	0.22	0.02	----	0.09	0.06	16
5/4/77 - 725	0.58	0.05	0.43	0.04	0.16	0.07	0.21	11
5/4/77 - 750	0.64	0.04	0.51	----	0.14	0.06	0.04	8
5/4/77 - 755	0187	0.21	5.24	0.02	0.84	----	----	2
5/4/77 - Passaic R. Fin. Water	32.28	----	29.96	1.77	0.40	0.06	----	7

(Continued)

TABLE 21. (Continued)

Sampling Date and Station	$CHCl_3$	CCl_4	$CHCl_2Br$	$CHClBr_2$ (µg/ℓ)	CCl_2CCl_2	$CHBr_3$	$CHCl_2CHCl_2$	UK*
5/13/77 - 100	0.89	----	0.55	----	0.62	----	----	1
5/13/77 - 120	1.06	0.03	0.47	0.02	0.52	----	----	3
5/13/77 - 130	0.38	0.02	0.04	----	0.01	----	----	1
5/13/77 - 165	0.55	0.05	0.26	0.04	0.05	----	----	3
5/13/77 - 175	0.41	0.02	0.11	----	0.02	----	----	1
5/13/77 - 180	0.41	0.02	0.05	----	0.02	----	----	1
5/13/77 - 210	1.68	0.04	0.25	----	2.28	----	----	2
5/13/77 - 280	0.92	0.04	0.40	----	1.30	----	----	3
5/13/77 - 285	0.53	0.01	0.17	----	0.38	----	----	3
5/13/77 - 310	0.51	0.02	0.13	----	0.05	----	----	3
5/13/77 - 805	0.74	0.05	1.00	0.11	0.30	0.12	----	3
5/13/77 - 810	0.53	0.02	0.14	----	0.05	----	----	3
5/13/77 - Passaic R. Fin. Water	14.62	0.10	26.89	1.21	0.72	----	----	4
5/13/77 - Wanaque R. Fin. Water	36.80	0.01	24.21	1.21	0.29	----	----	4
5/13/77 - Mixed Fin. Water	33.92	0.07	22.21	1.02	0.48	----	----	4

*UK is the number of unidentified ECD Peaks.

TABLE 21. (Continued)

Sampling Date and Station	$CHCl_3$	CCl_4	$CHCl_2Br$	$CHClBr_2$ (µg/ℓ)	CCl_2CCl_2	$CHBr_3$	$CHCl_2CHCl_2$	UK*
5/13/77 - 100	0.89	----	0.55	----	0.62	----	----	1
5/13/77 - 120	1.06	0.03	0.47	0.02	0.52	----	----	3
5/13/77 - 130	0.38	0.02	0.04	----	0.01	----	----	1
5/13/77 - 165	0.55	0.05	0.26	0.04	0.05	----	----	3
5/13/77 - 175	0.41	0.02	0.11	----	0.02	----	----	1
5/13/77 - 180	0.41	0.02	0.05	----	0.02	----	----	1
5/13/77 - 210	1.68	0.04	0.25	----	2.28	----	----	2
5/13/77 - 280	0.92	0.04	0.40	----	1.30	----	----	3
5/13/77 - 285	0.53	0.01	0.17	----	0.38	----	----	3
5/13/77 - 310	0.51	0.02	0.13	----	0.05	----	----	3
5/13/77 - 805	0.74	0.05	1.00	0.11	0.30	0.12	----	3
5/13/77 - 810	0.53	0.02	0.14	----	0.05	----	----	3
5/13/77 - Passaic R. Fin. Water	14.62	0.10	26.89	1.21	0.72	----	----	4
5/13/77 - Wanaque R. Fin. Water	36.80	0.01	24.21	1.21	0.29	----	----	4
5/13/77 - Mixed Fin. Water	33.92	0.07	22.21	1.02	0.48	----	----	4

*UK is the number of unidentified ECD Peaks.

TABLE 22. TRIHALOMETHANE FORMATION POTENTIAL OF STREAM SAMPLES* TAKEN 5/4/77

Station No.	Initial pH	THMFP µg/ℓ	Station No.	Initial pH	THMFP µg/ℓ
106-B	7.2	20.3	540	7.1	65.5
610	7.1	93.0	100	7.1	89.2
110	7.1	98.6	120	7.1	141.0
115	7.1	133.1	310	7.1	118.9
630	7.0	94.7	210	7.1	95.5
660	7.1	95.4	130	7.0	134.8
410	7.2	66.5	165	7.1	233.5
510	7.0	98.9	175	7.6	282.4
670	7.0	87.1	810	7.2	71.5
710	6.9	90.9	805	7.5	78.0
725	6.9	78.2	180	7.5	79.0
750	6.9	102.1	280	7.0	80.5
755	7.0	66.9	285	7.0	107.4

*Trihalomethane Formation Potential (THMFP) is the sum of the concentrations of the following compounds: $CHCl_3$, $CHCl_2Br$, $CHCLBr_2$, $CHBr_3$. Conditions used were 20 ppm Cl_2 reaction time three hours.

The numbers indicated above are those employed in Tables 23 to 25.

Table 23 lists the volatile halogenated solvent concentrations determined on quenched ($Na_2S_2O_3$ added) samples collected on 3/1/78. Table 24 lists the volatile halogenated solvent concentrations determined on samples collected on 3/1/78 and held for seven days at 20°C. The Passaic River intake sample was not chlorinated and was used as a control. Table 25 lists the total trihalomethane formation potentials for all samples collected 3/1/78. Table 26 indicates the extent of the trihalomethane formation in the quenched samples. In addition to the halogenated solvents listed, a large unknown component was noted only in chlorinated Passaic River finished water. Its retention time was 0.10 minutes later than 1,1,2-trichloroethane and its concentration calculated as 1,1,2-trichloroethane was 186 ppb in the Passaic River finished water.

From the information contained in Table 26 it is evident that at the time of sampling there was a larger concentration of THM precursors present in the Wanaque raw supply as compared to the Passaic River raw supply. After seven days of storage at 20°C, treated water from the Wanaque supply exhibited a larger THM value. This problem is compounded by the fact that a chlorine dosage of 30 ppm was applied to the Passaic supply in efforts to break-point chlorinate and only 3 ppm of chlorine was applied to the Wanaque supply. The observed THM concentration in distribution system samples only reach a value of approximately one-half that of the value obtained on the same treated water stored for seven days at 20°C. This would indicate that TTHMFP values obtained by the storage method should be interpreted with caution and provide a poor correlation to actual distribution THM observed values.

C. TRIHALOMETHANE FORMATION CURVES FOR STREAM SAMPLES

A series of chlorination experiments were conducted to determine the shape of the trihalomethane kinetic formation curve. Table 27 lists the streams that were sampled and their chlorine dosages. Conditions of the chlorination procedure and subsequent analysis of trihalomethanes are briefly described below.

A 1.6 liter aliquot of each stream sample was added to a 2 liter volumetric flask. To this, 1 ml of hypochlorite solution was added to yield a final concentration of 10 mg/l free chlorine. The sample volume was adjusted to 2 liters with additional stream water. The volumetric flask was agitated by hand and an initial sample was withdrawn (time = 0) and quenched with $Na_2S_2O_3$. Ten additional 150 ml samples were withdrawn for each stream chlorination run and sealed with a Teflon septa. Chlorinated samples were stored at 20°C (in the absence of light) until ready for analysis.

Sampling times, in hours, for all stream chlorination runs were as follows: 0, 3, 24, 54, 80, 144, 168, and 264 hr. The procedure at each time interval was to measure the free chlorine content (DPD/colormetric) and then to quench with $Na_2S_2O_3$. The quenched sample was extracted with n-pentane. The extract was subjected to capillary column gas chromatography for analysis

TABLE 23. INSTANTANEOUS TRIHALOMETHANE ANALYSIS RESULTS FOR SAMPLES COLLECTED 3/1/78 (CONCENTRATIONS ARE FOR AVERAGE OF THREE RUNS)

Compound Site*	$CHCl_3$ µg/ℓ	CH_3CCl_3 µg/ℓ	CCL_4 µg/ℓ	$CHCl_2Br_2$ µg/ℓ	$CHClBr_2$ µg/ℓ	CCl_2CCl_2 µg/ℓ	$CHBr_3$ µg/ℓ
1	2.11	2.84	0.14	1.03	----	2.49	----
	±0.12	±0.54	±0.01	±0.05	----	±0.06	----
2	46.30	0.78	---	9.62	0.49	----	----
	±1.42	±0.39	---	±0.37	±0.02	----	----
3	48.45	0.45	---	9.85	0.49	----	----
	±1.54	±0.02	---	±0.32	±0.01	----	----
4	40.42	2.68	0.51	15.14	1.18	2.31	0.29
	±0.99	±0.32	±0.01	±0.34	±0.03	±0.05	±0.01
5	45.82	1.47	0.25	13.15	0.85	0.99	----
	±1.89	±0.33	±0.01	±0.46	±0.02	±0.03	----
6	56.55	2.70	0.46	24.54	2.23	2.06	0.36
	±0.77	±0.13	±0.01	±0.06	±0.0005	±0.02	±0.02
7	55.31	1.76	0.40	23.92	1.74	1.81	0.33
	±1.98	±0.09	±0.02	±0.83	±0.08	±0.09	±0.04
8	57.12	0.98	0.25	19.91	1.19	0.98	----
	±1.92	±0.27	±0.004	±0.63	±0.05	±0.02	----

TABLE 24. TERMINAL TRIHALOMETHANE ANALYSIS (7 DAYS AT 20°C) FOR SAMPLES COLLECTED 3/1/78 (AVERAGE OF THREE RUNS)

Site	Compound $CHCl_3$ µg/ℓ	CCl_3CH_3 µg/ℓ	CCl_4 µg/ℓ	$CHCl_2Br$ µg/ℓ	$CHClBr_2$ µg/ℓ	CCl_2CCl_2 µg/ℓ	$CHBr_3$ µg/ℓ
1	2.57	25.66	0.15	1.05	---	2.61	---
	±0.32	± 5.69	±0.02	±0.09	---	±0.27	---
2	160.65	17.75	0.13	23.38	0.99	0.28	---
	±2.36	±0.72	±0	±0.28	±0.01	±0.01	---
3	175.15	30.17	0.13	25.13	1.06	0.30	
	±3.59	±1.72	±0.01	±0.40	±0.02	±0.004	---
4	104.7	19.33	0.59	38.79	4.02	2.59	0.51
	±0.70	±0.19	±0.01	±0.19	±0.01	±0.02	±0.05
5	119.73	14.09	0.32	29.85	1.81	1.02	2.24
	±1.94	±0.32	±0.01	±0.30	±0.02	±1.01	±0.76
6	110.84	17.97	0.53	37.88	3.77	2.17	0.42
	±0.61	±1.68	±0.01	±0.11	±0.03	±0.04	±0.01
7	103.26	14.01	0.43	34.34	2.76	1.78	0.32
	±4.24	±2.85	±0.01	±1.18	±0.19	±0.04	±0.02
8	88.98	20.58	0.27	24.94	1.53	0.91	0.83
	±3.58	±9.42	±0.02	1±.37	±0.08	±0.03	±0.12

TABLE 25. TOTAL TRIHALOMETHANE FORMATION POTENTIAL OF SAMPLES COLLECTED 3/1/78

Site	ITHM* µg/ℓ	TTHM† µg/ℓ	TTHMFP‡‡ µg/ℓ
1	2.13	2.62	0.48
2	56.41	185.02	147.85
3	58.79	201.34	147.55
4	57.30	148.02	90.72
5	59.82	153.63	93.81
6	83.73	152.91	69.18
7	81.30	140.68	59.38
8	78.22	116.28	38.06

* ITHM = Instantaneous total trihalomethane concentration

† Terminal total trihalomethane concentration (sample stored for seven days at 20°C).

‡‡ TTHMFP = Total trihalomethane formation potential (TTHM - ITHM)

TABLE 26. EXTENT OF TERMINAL TRIHALOMETHANE FORMATION FOR QUENCHED SAMPLES* COLLECTED 3/1/78

Site	% of TTHMFP
1	81.3
2	30.5
3	29.2
4	38.7
5	38.9
6	54.8
7	57.8
8	67.3

*Instantaneous total trihalomethane analysis quenched with $Na_2S_2O_3$

TABLE 27. STREAM SAMPLE CHLORINATION INFORMATION

Sampling Station	Sampling Date	Chlorine Added* ppm	pH
230	1/6/78	10	6.9
530	1/6/78	10	7.0
610	1/6/78	10	6.9
180	1/6/78	10	6.9
810	1/6/78	60†	6.9
Wanaque Reservoir	1/6/78	10	6.8
725	1/6/78	10	7.0
310	1/6/78	10	6.6
100	1/6/78	10	6.7
440	1/6/78	10	6.6

* Measured by DPD/colormetric method

† Initial chlorine concentration = 10ppm with 50 ppm added after 24 hours

as detailed in Section 4. Figures 15 through 34 illustrate results for the exhaustive chlorination of stream samples.

One sample (Dead River) exhausted free chlorine after 24 hours of incubation, and required the addition of 50 ppm free chlorine to maintain free chlorine residual throughout the sampling period.

The general trend in the kinetic formation plots for the trihalomethane was a first order rate of formation. The upper reaches of the Passaic River. especially the Dead River, exhibited a large concentration of chloroform at the termination of the curve (approximately 250-300 ppb). The Wanaque River and Reservoir also exhibited this behavior. It is interesting to note that in all samples except one (Whippany River) the free chlorine concentration curve exhibited at least one inflection point, indicating a secondary oxidation, perhaps the final cleavage of certain chlorinated precursors to form THMS.

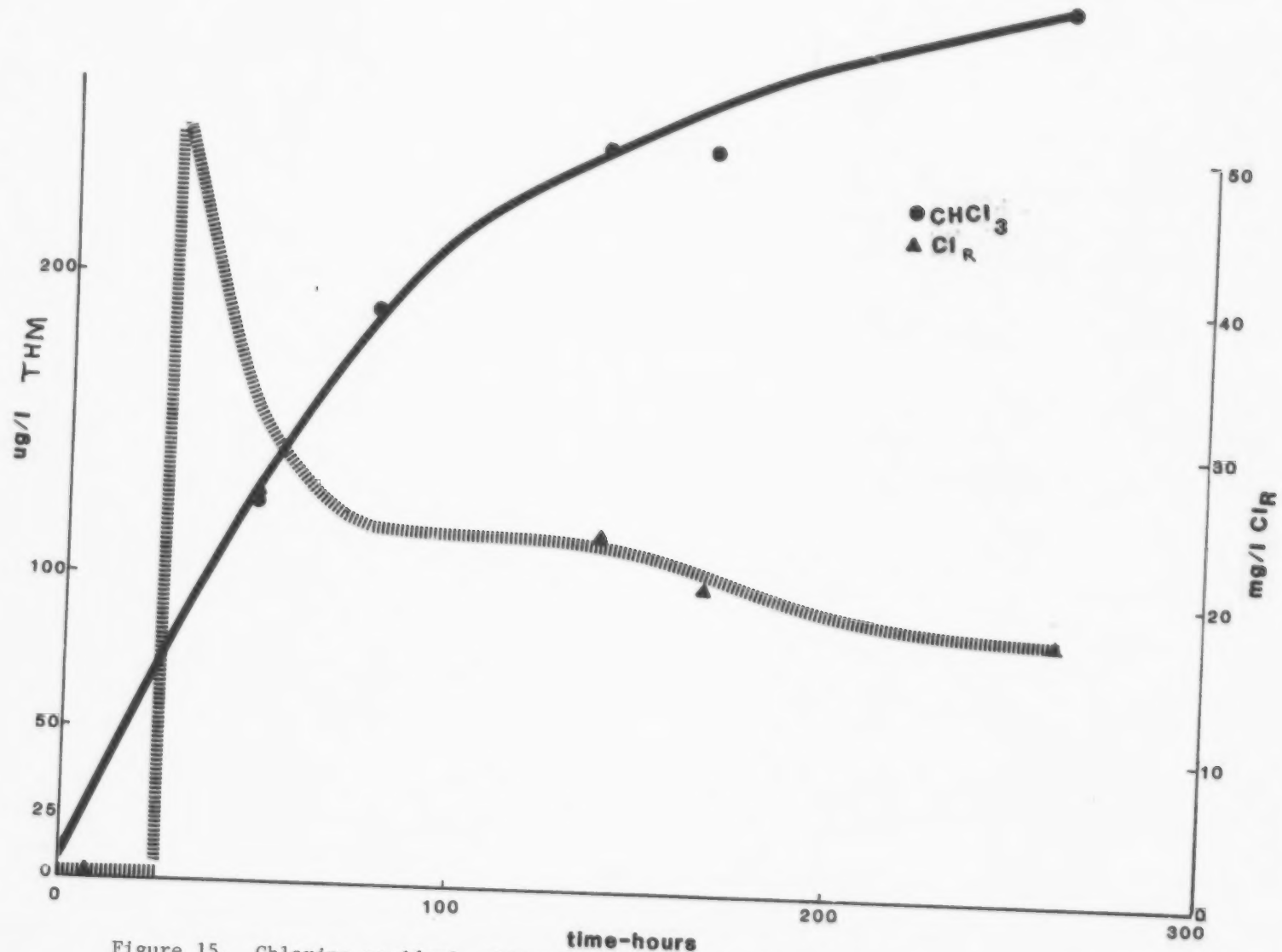

Figure 15. Chlorine residual, chloroform and dichlorobromomethane concentrations in chlorinated Dead River water (Station 810).

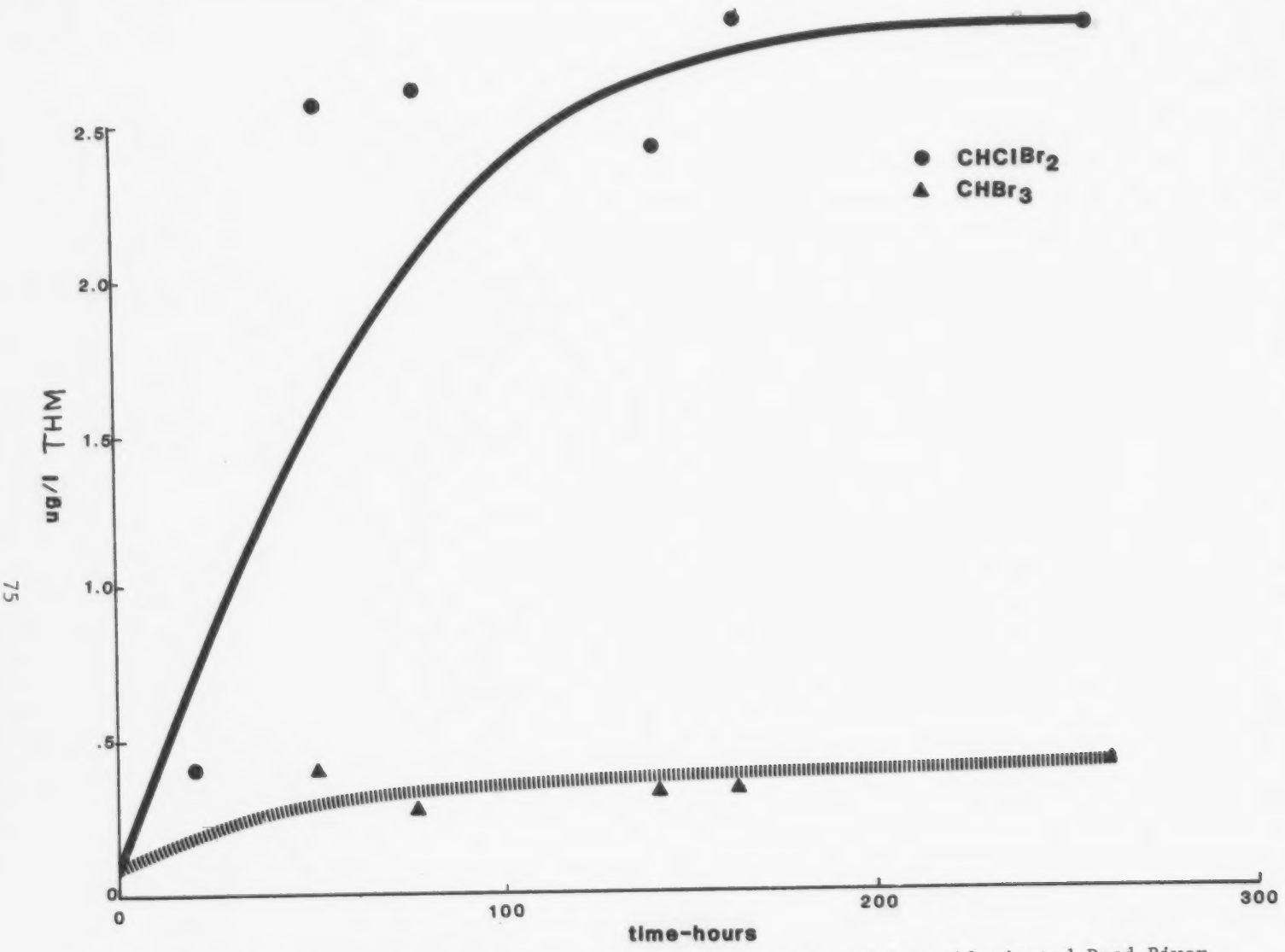

Figure 16. Dibromochloromethane and bromoform concentrations in chlorinated Dead River water (Station 810).

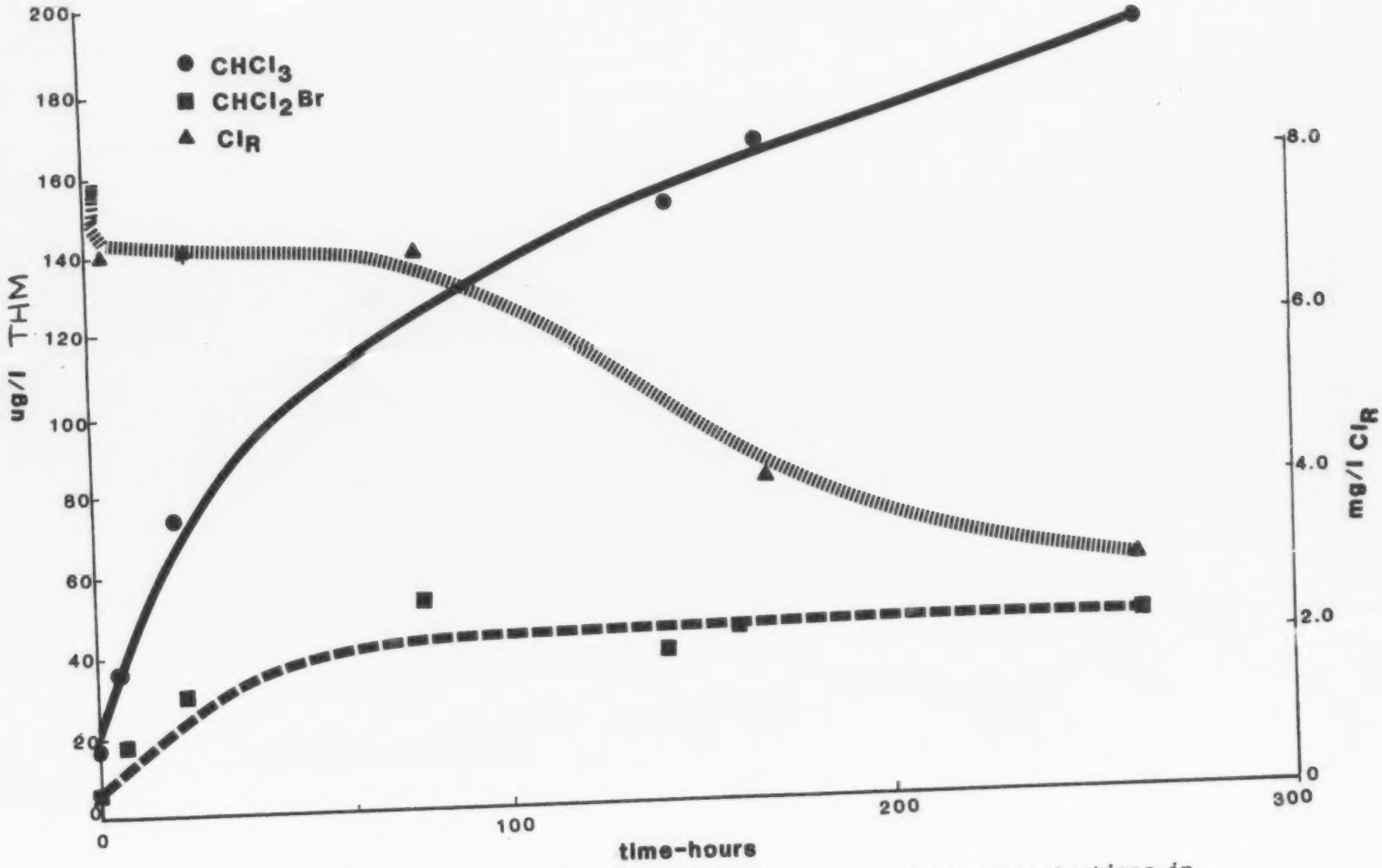

Figure 17. Chlorine residual, chloroform and dichlorobromomethane concentrations in chlorinated Pequannock River water (Station 440).

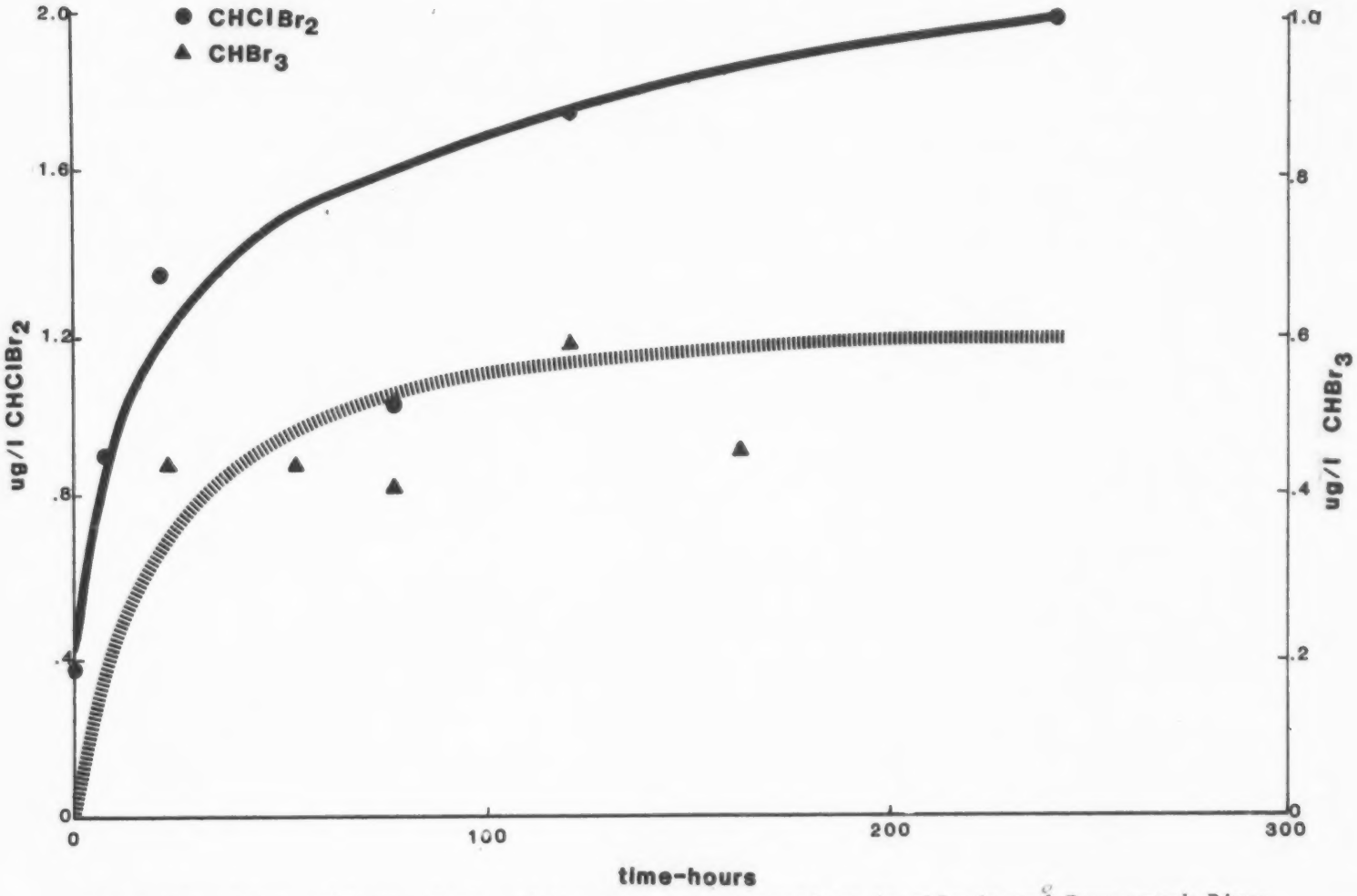

Figure 18. Dibromochloromethane and bromoform concentrations in chlorinated Pequannock River water (Station 440).

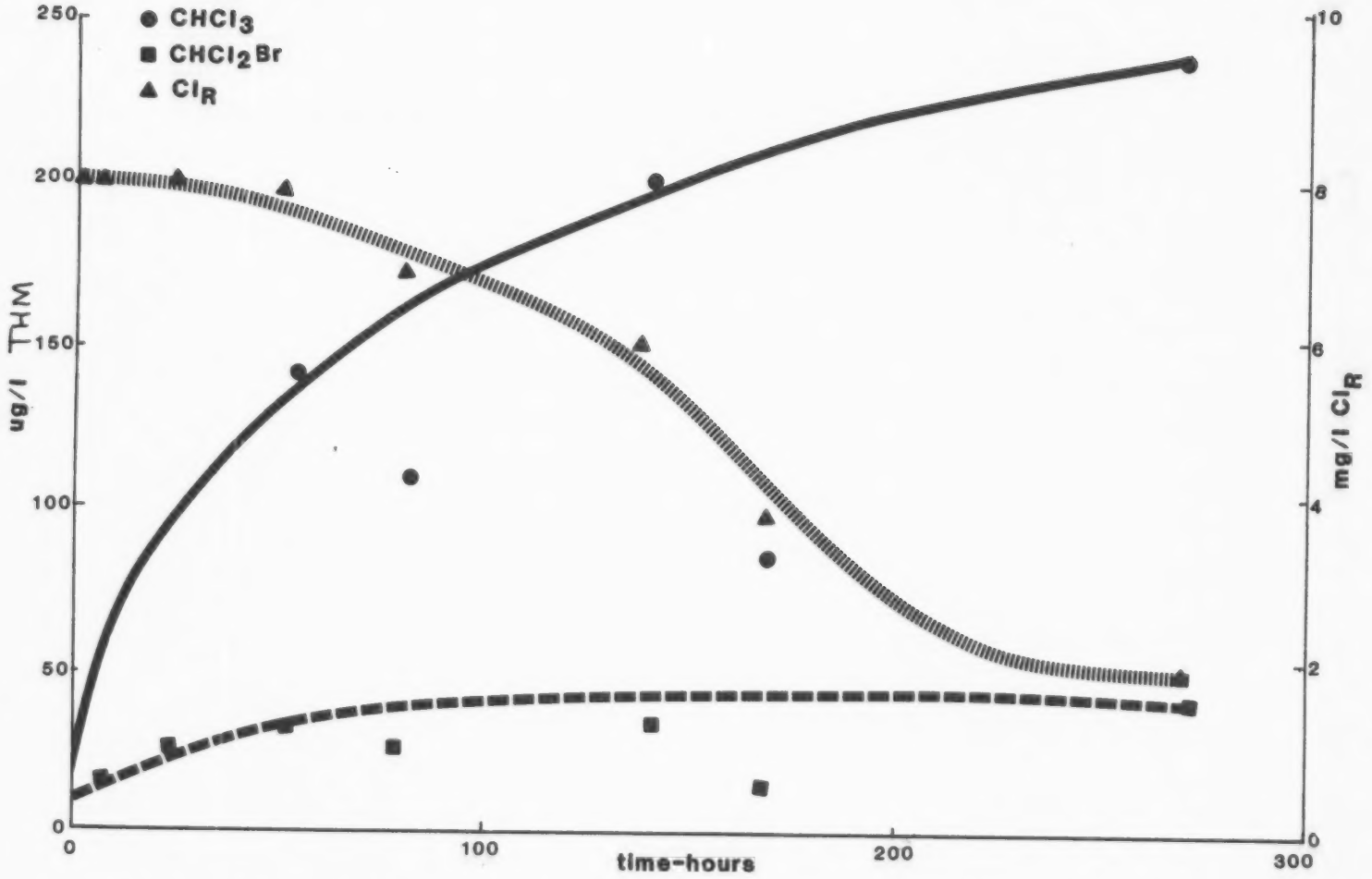

Figure 19. Chlorine residual, chloroform and dichlorobromomethane concentrations in chlorinated Pompton River water (Station 610).

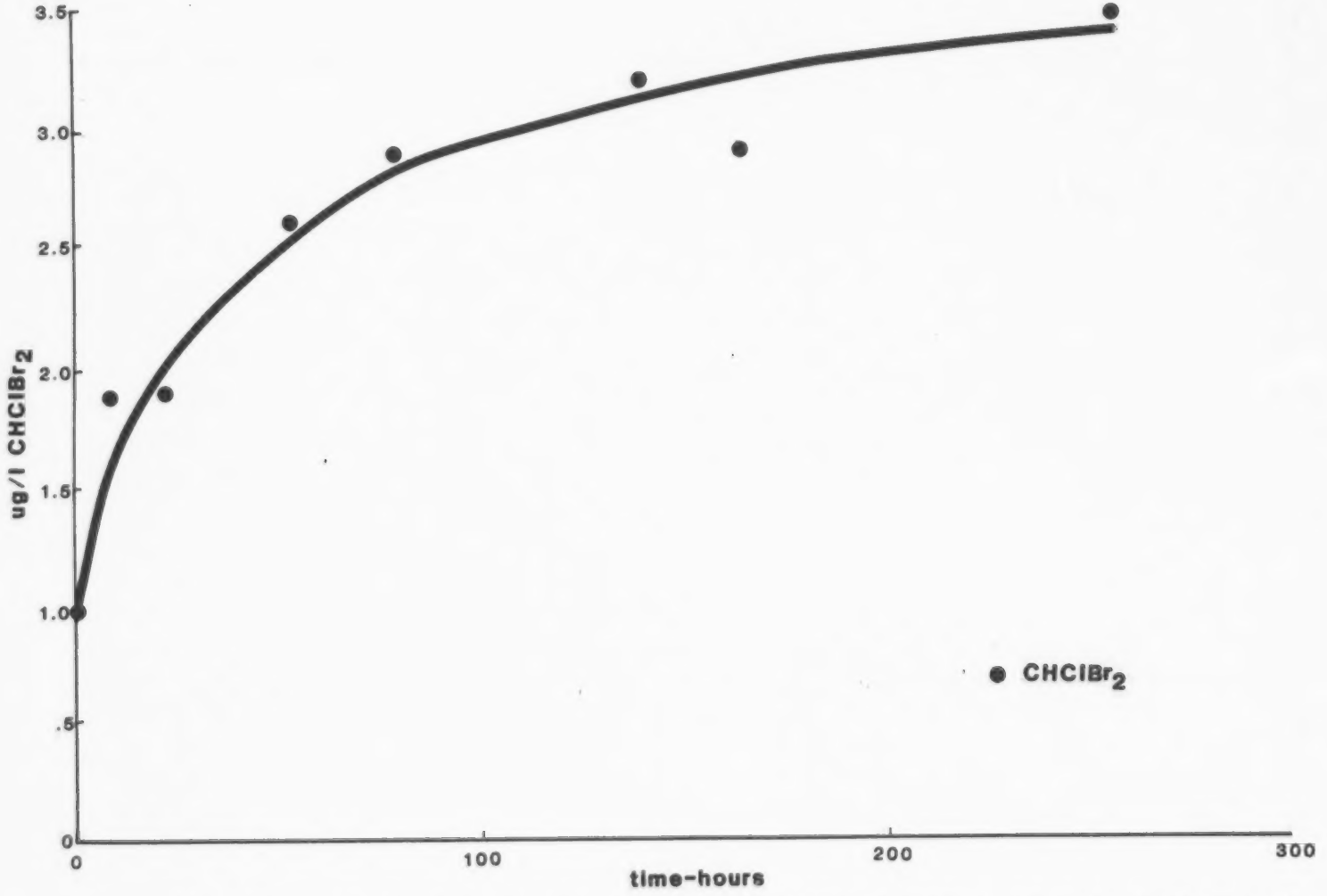

Figure 20. Dibromochloromethane concentrations in chlorinated Pompton River water (Station 610).

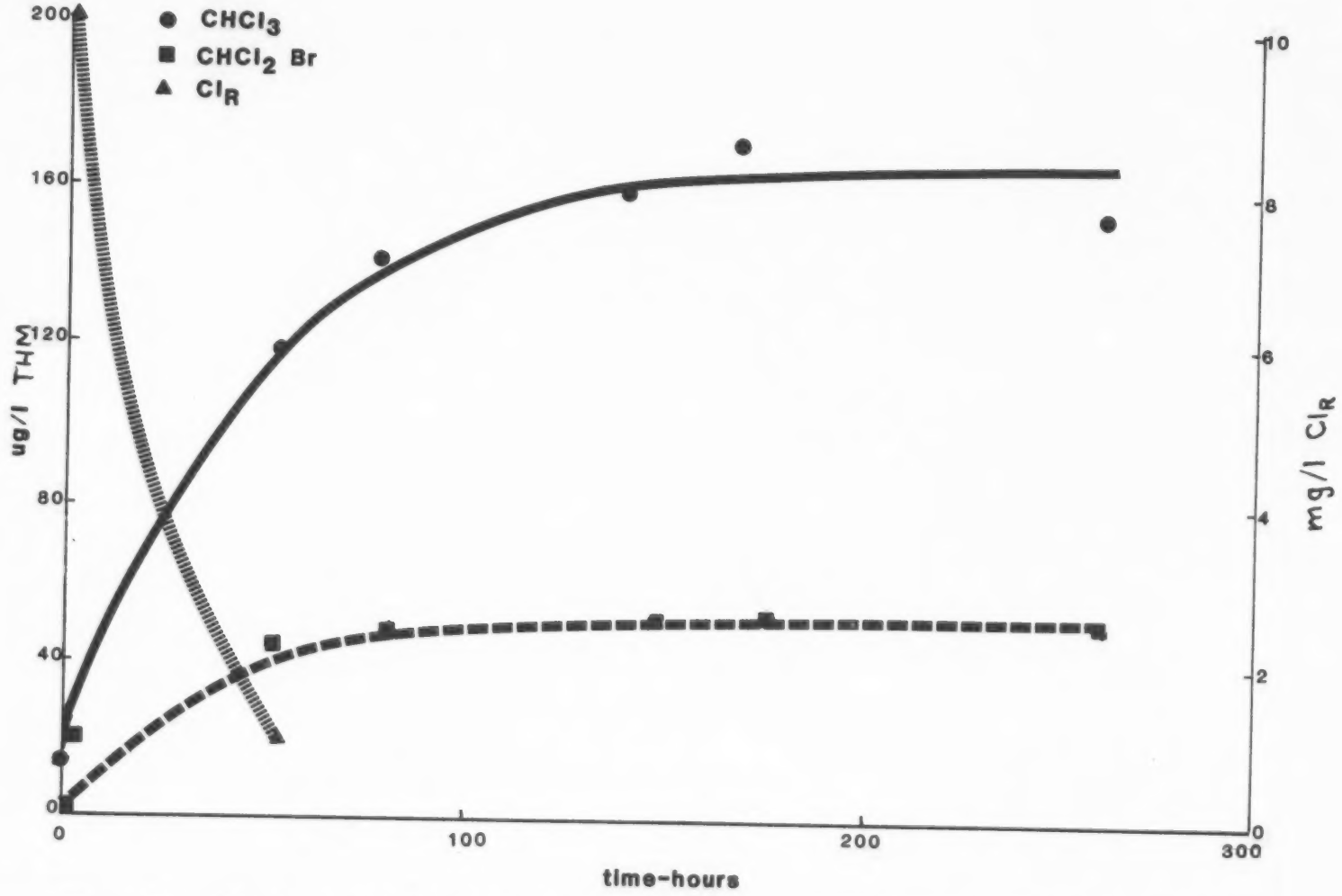

Figure 21. Chlorine residual, chloroform and dichlorobromomethane concentrations in chlorinated Whippany River water (Station 230).

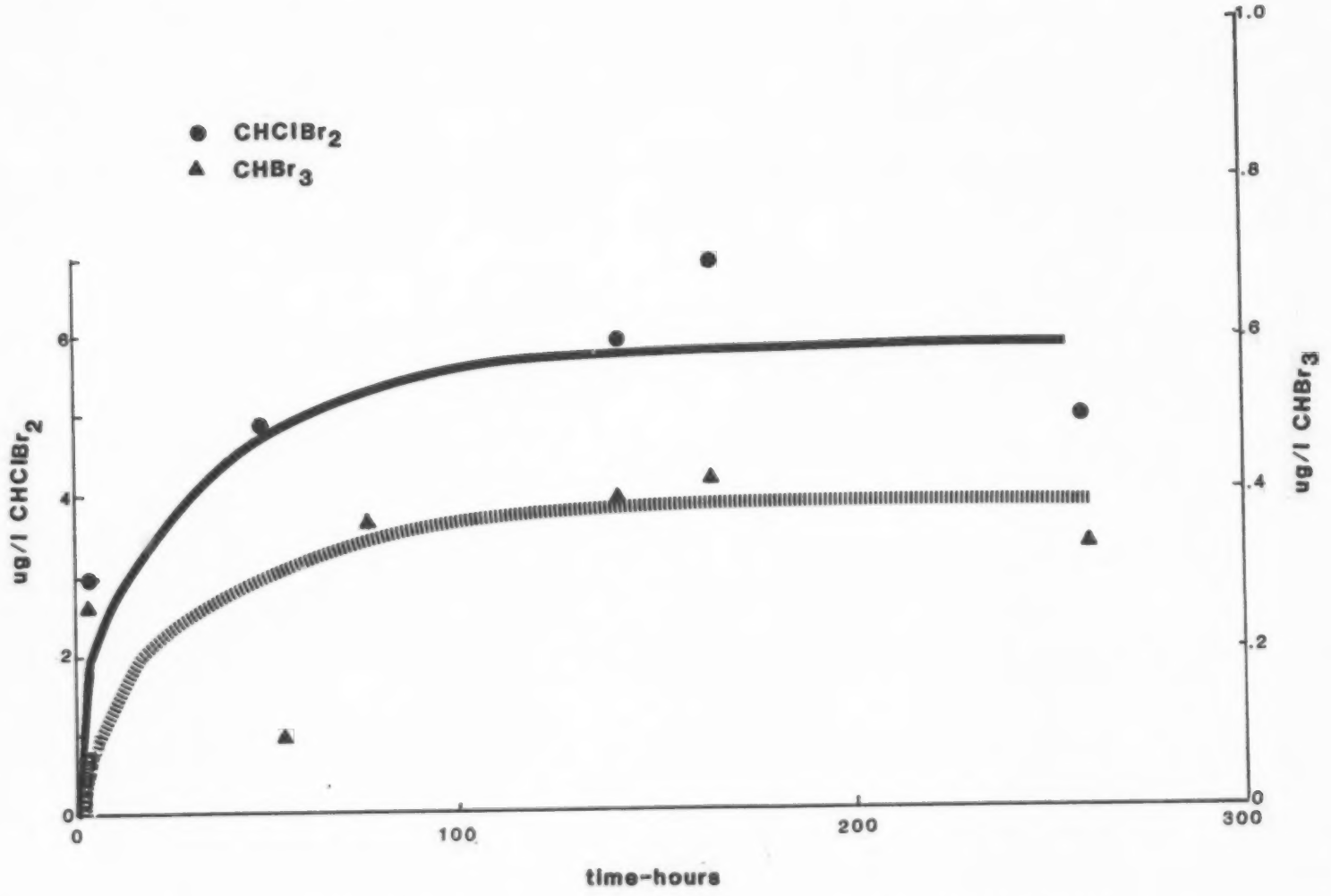

Figure 22. Dibromochloromethane and bromoform concentrations in chlorinated Whippany River water (Station 230).

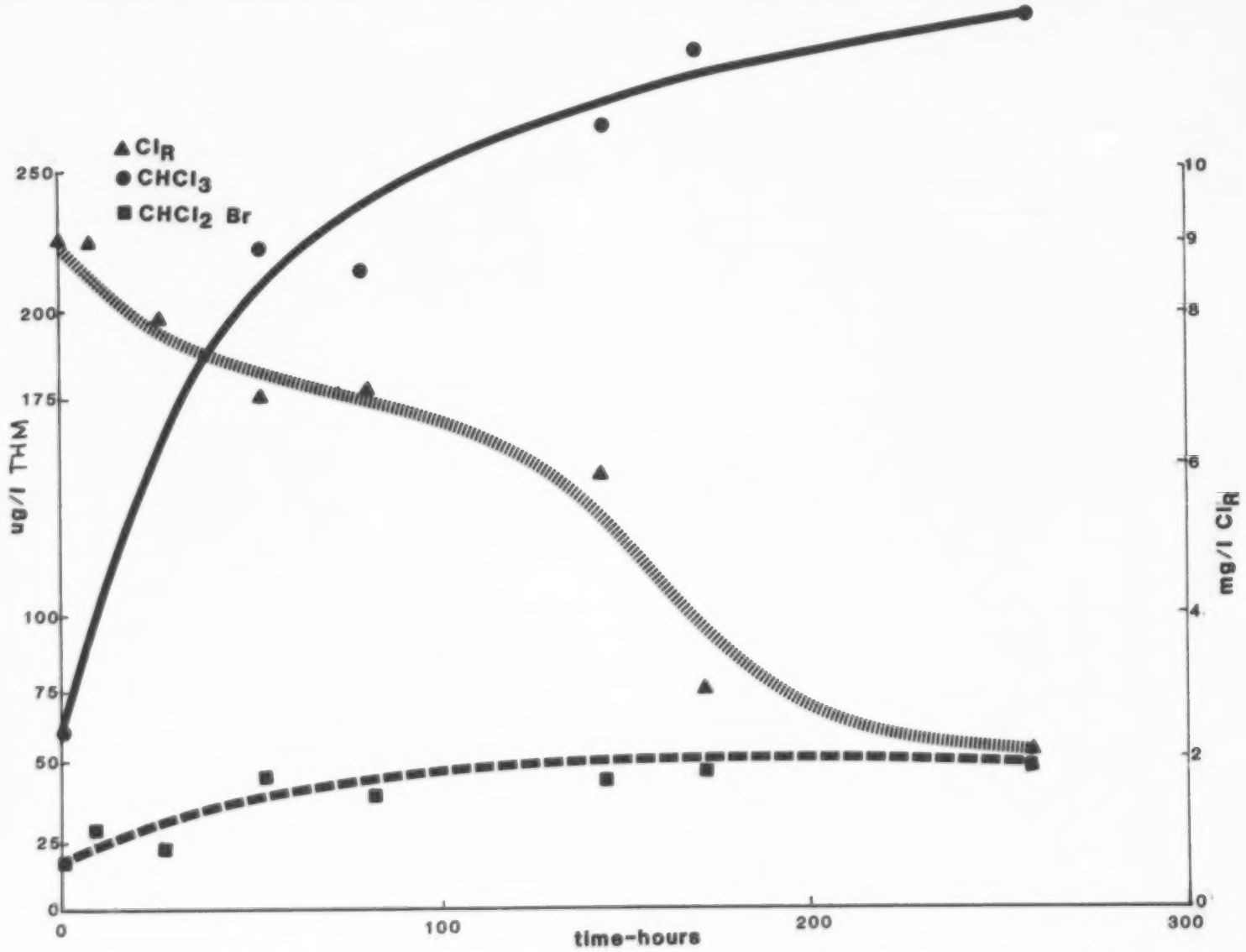

Figure 23. Chlorine residual, chloroform and dichlorobromomethane concentrations in chlorinated Rockaway River water (Station 310).

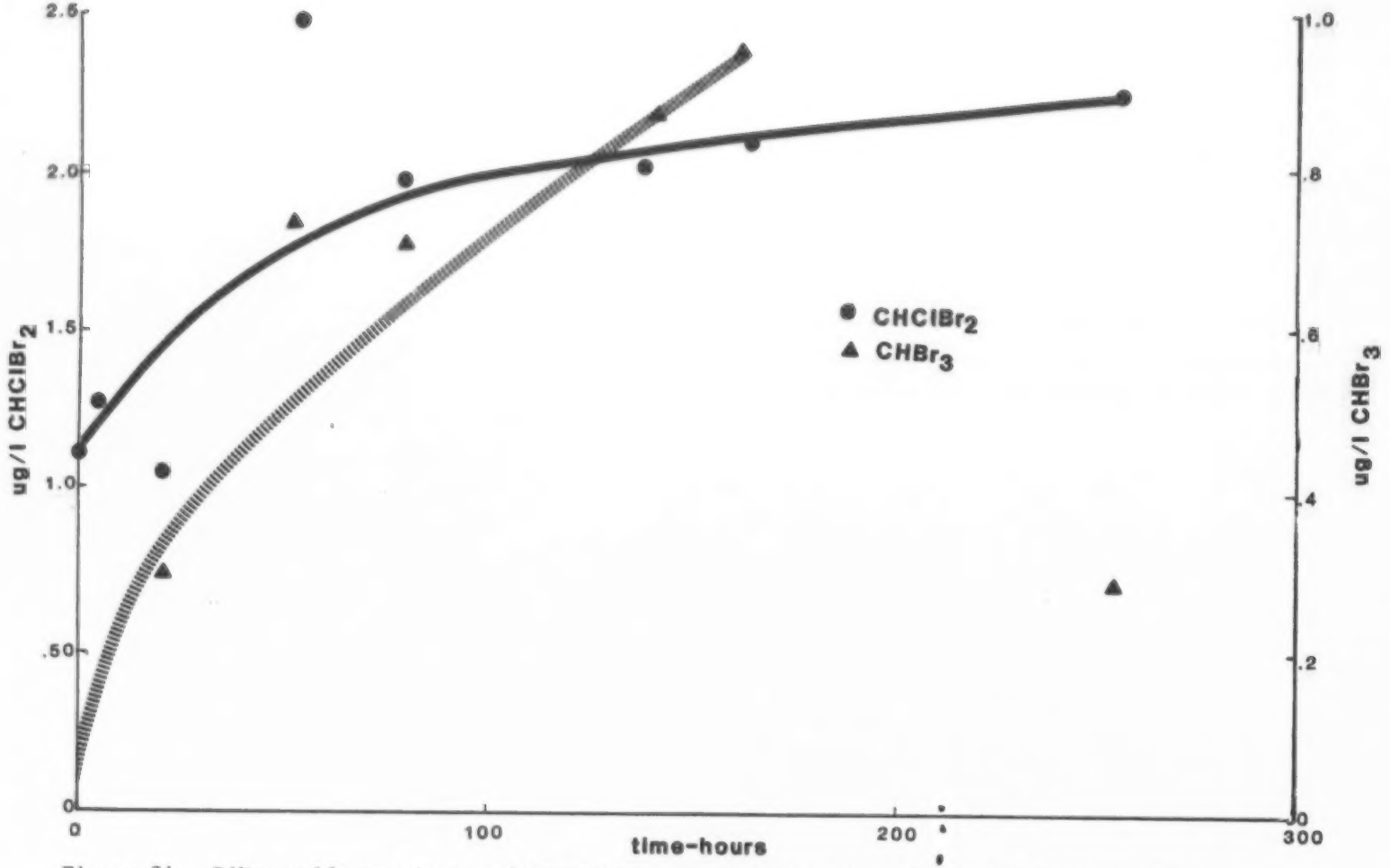

Figure 24. Dibromochloromethane and bromoform concentrations in chlorinated Rockaway River water (Station 310).

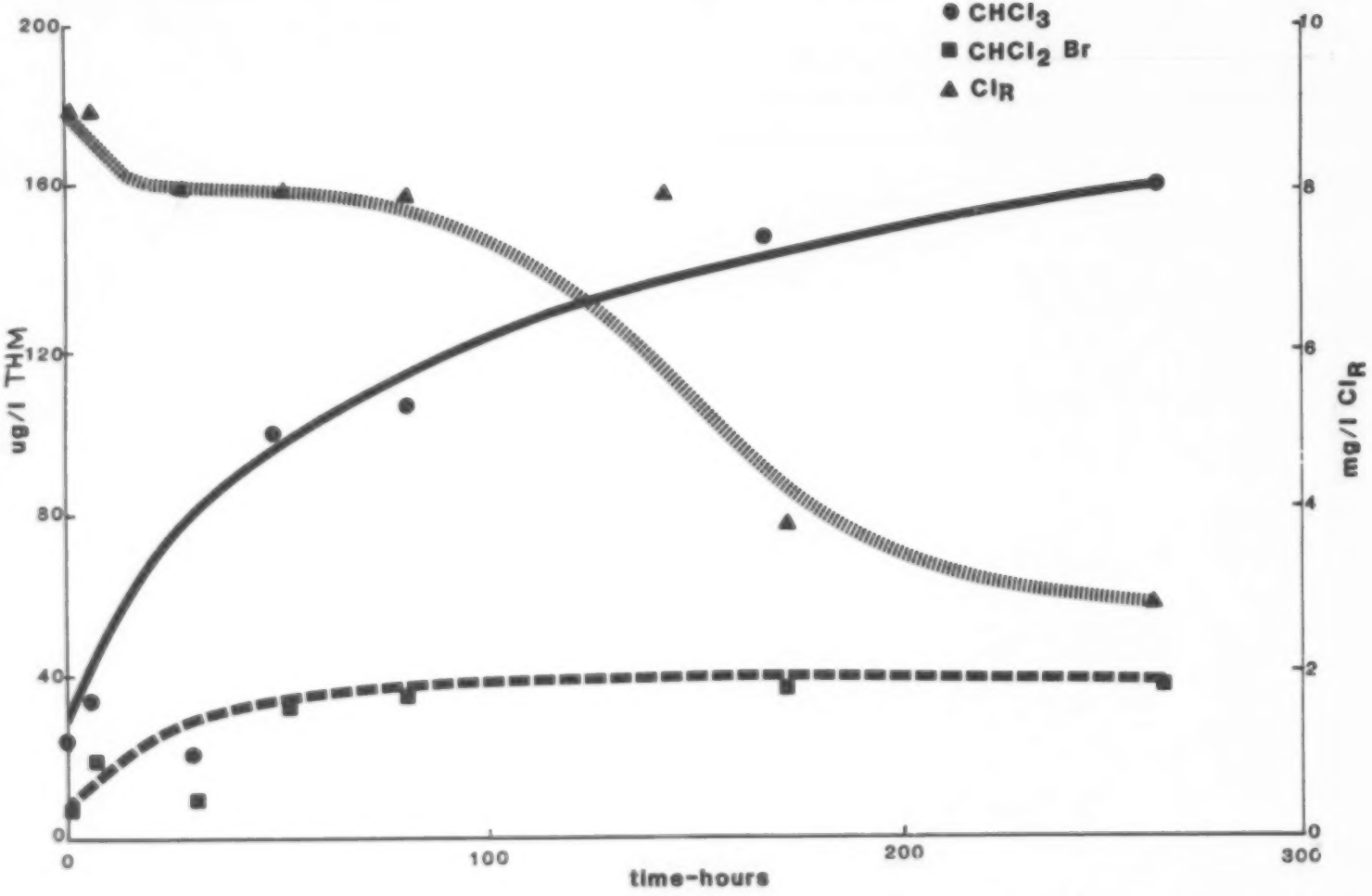

Figure 25. Chlorine residual, chloroform and dichlorobromomethane concentrations in chlorinated Ramapo River water (Station 725).

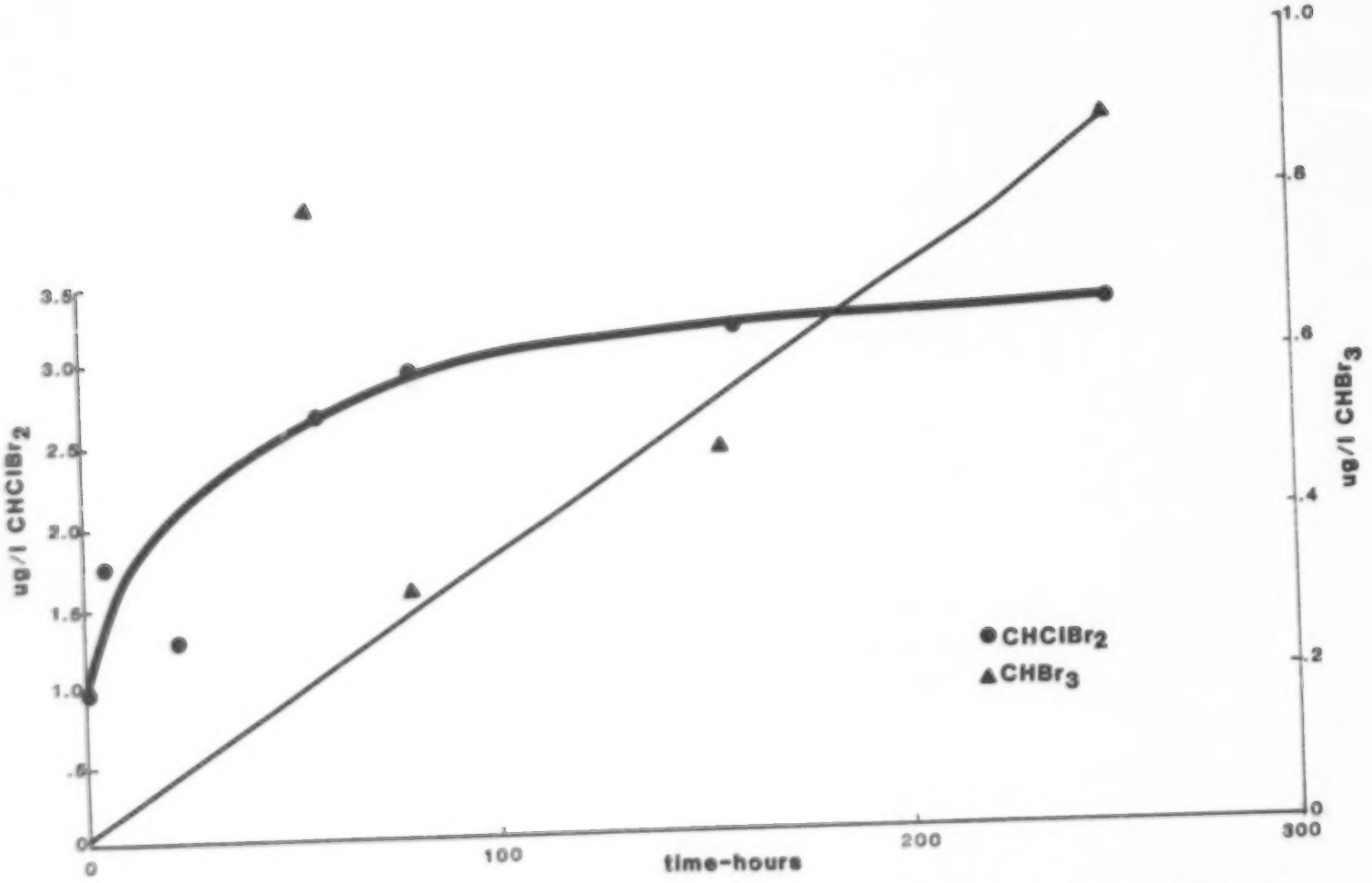

Figure 26. Dibromochloromethane and bromoform concentrations in chlorinated Ramapo River water (Station 725).

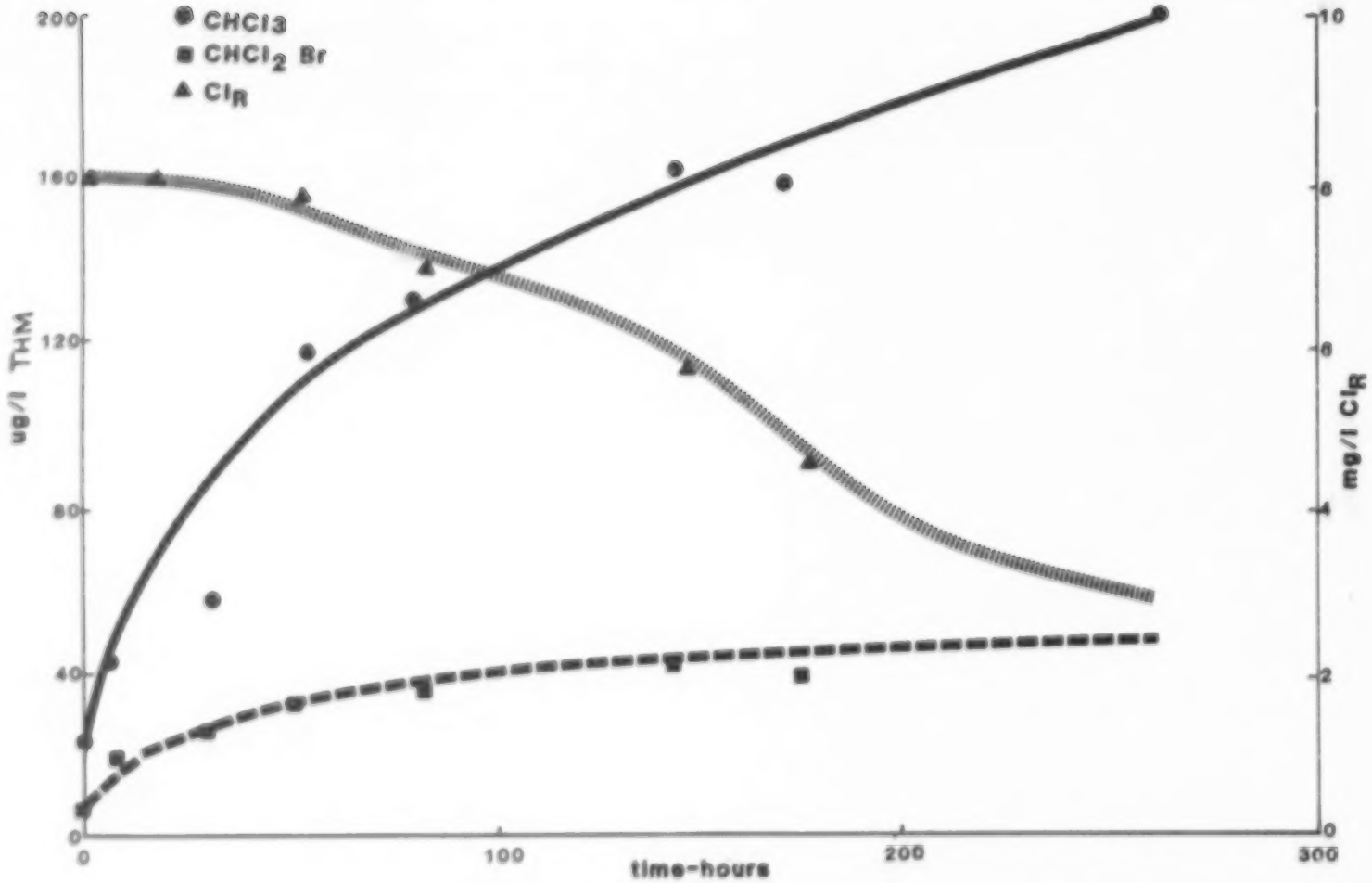

Figure 27. Chlorine residual, chloroform and dichlorobromomethane concentrations in chlorinated Wanaque River water (Station 530).

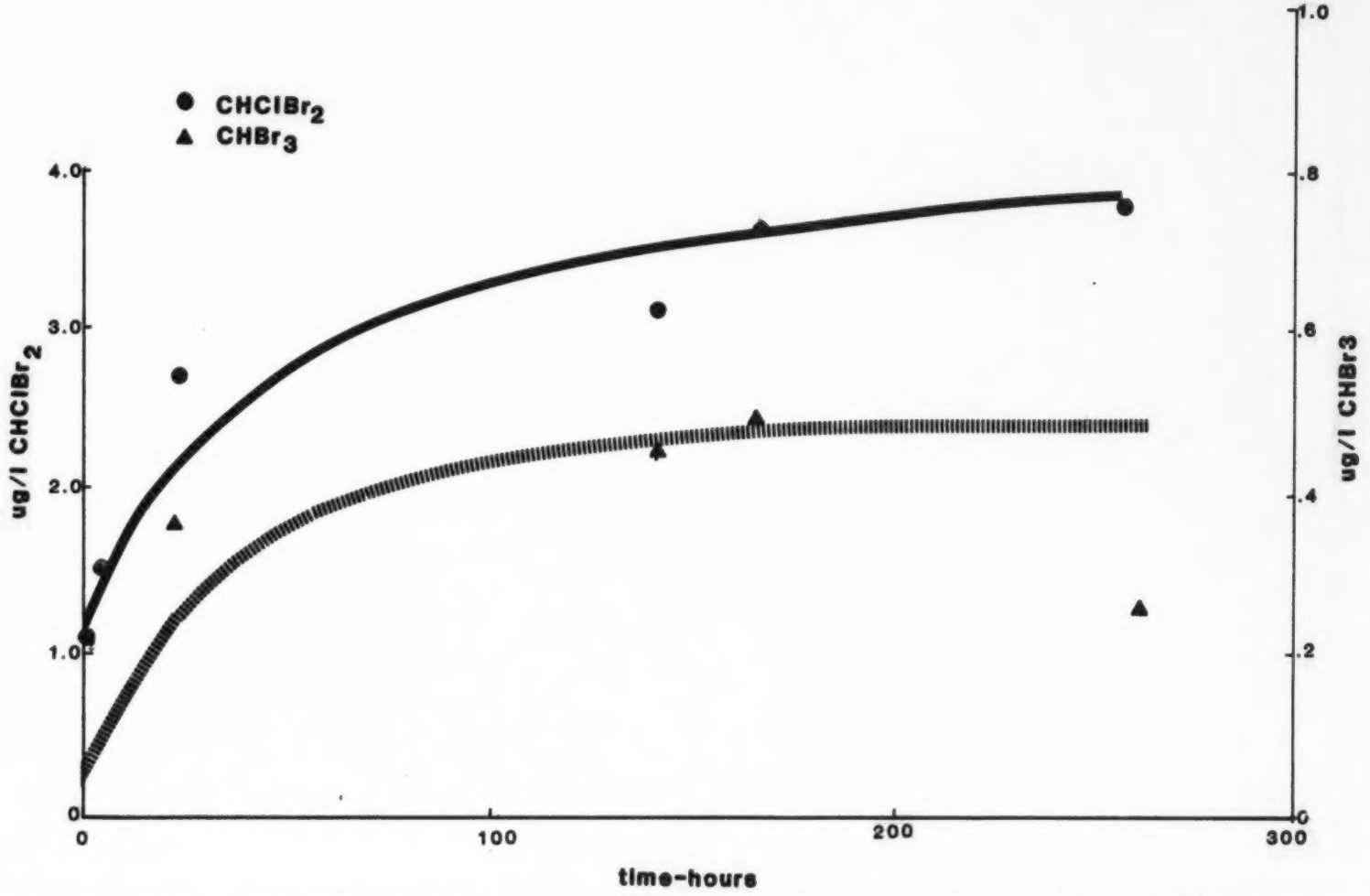

Figure 28. Dibromochloromethane and bromoform concentrations in chlorinated Wanaque River water (Station 530).

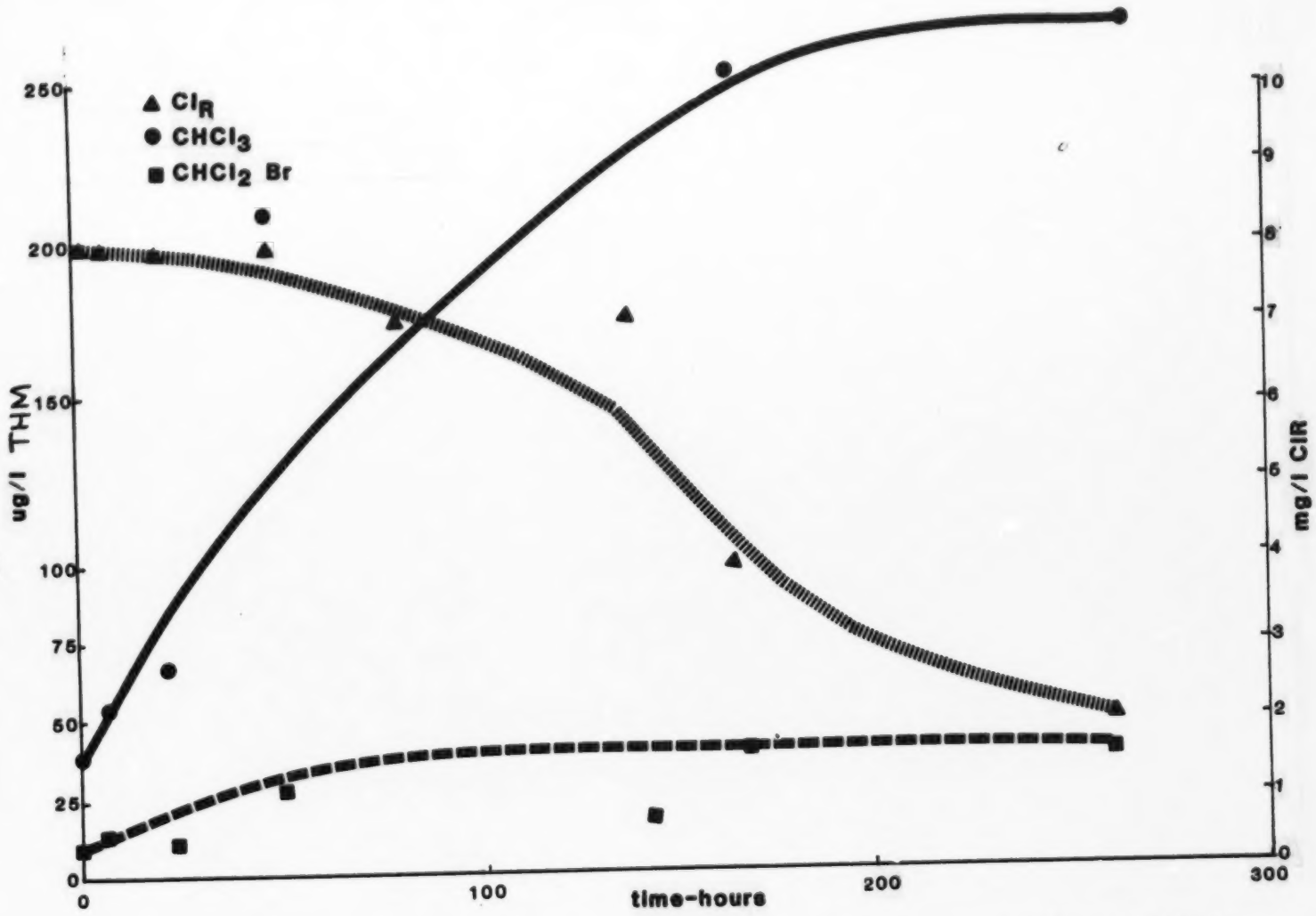

Figure 29. Chlorine residual, chloroform and dichlorobromomethane concentrations in chlorinated Wanaque Reservoir water.

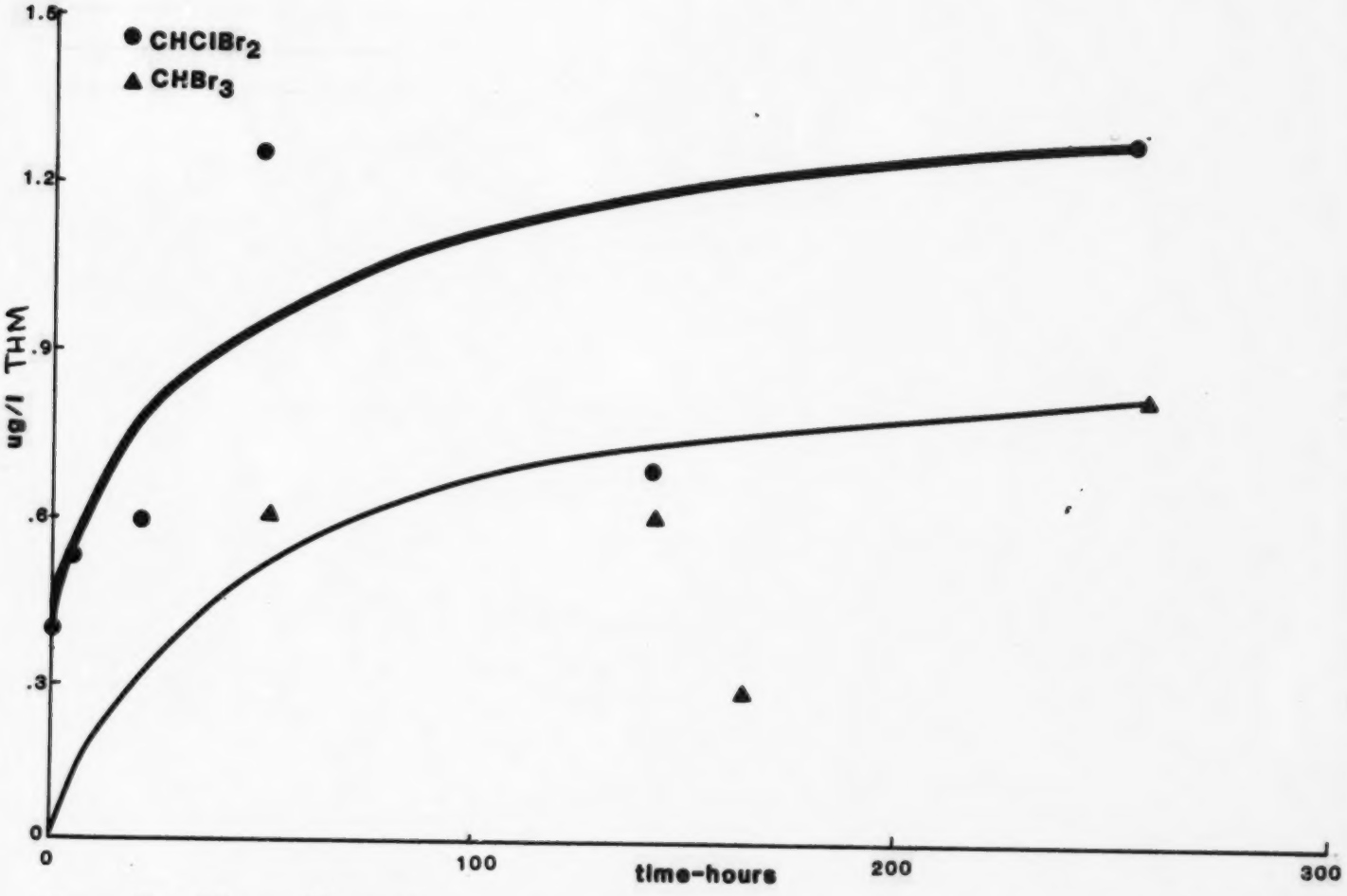

Figure 30. Dibromochloromethane and bromoform concentrations in chlorinated Wanaque Reservoir water.

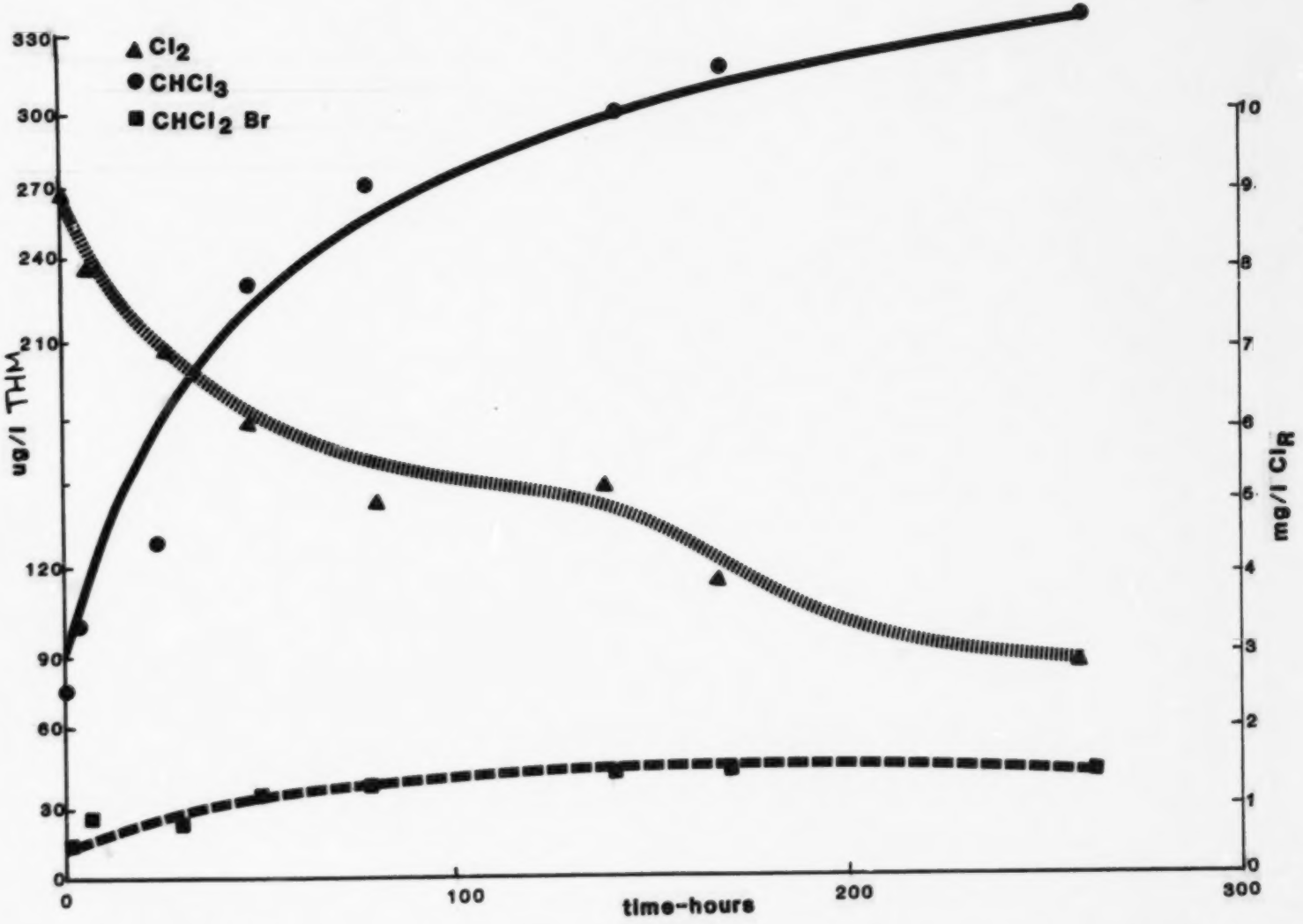

Figure 31. Chlorine residual, chloroform and dichlorobromomethane concentrations in Upper Passaic River water (Station 180).

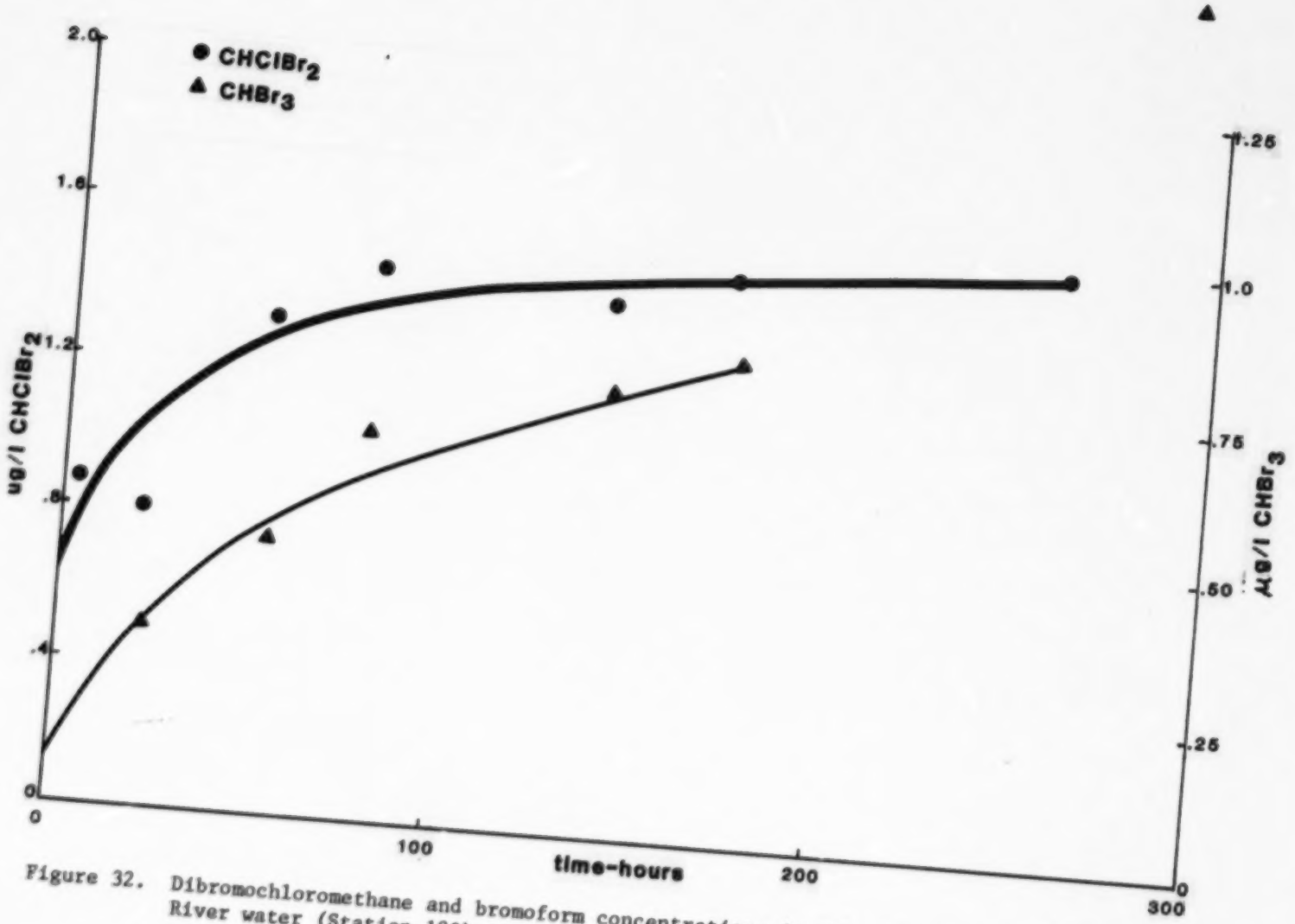

Figure 32. Dibromochloromethane and bromoform concentrations in chlorinated Upper Passaic River water (Station 180).

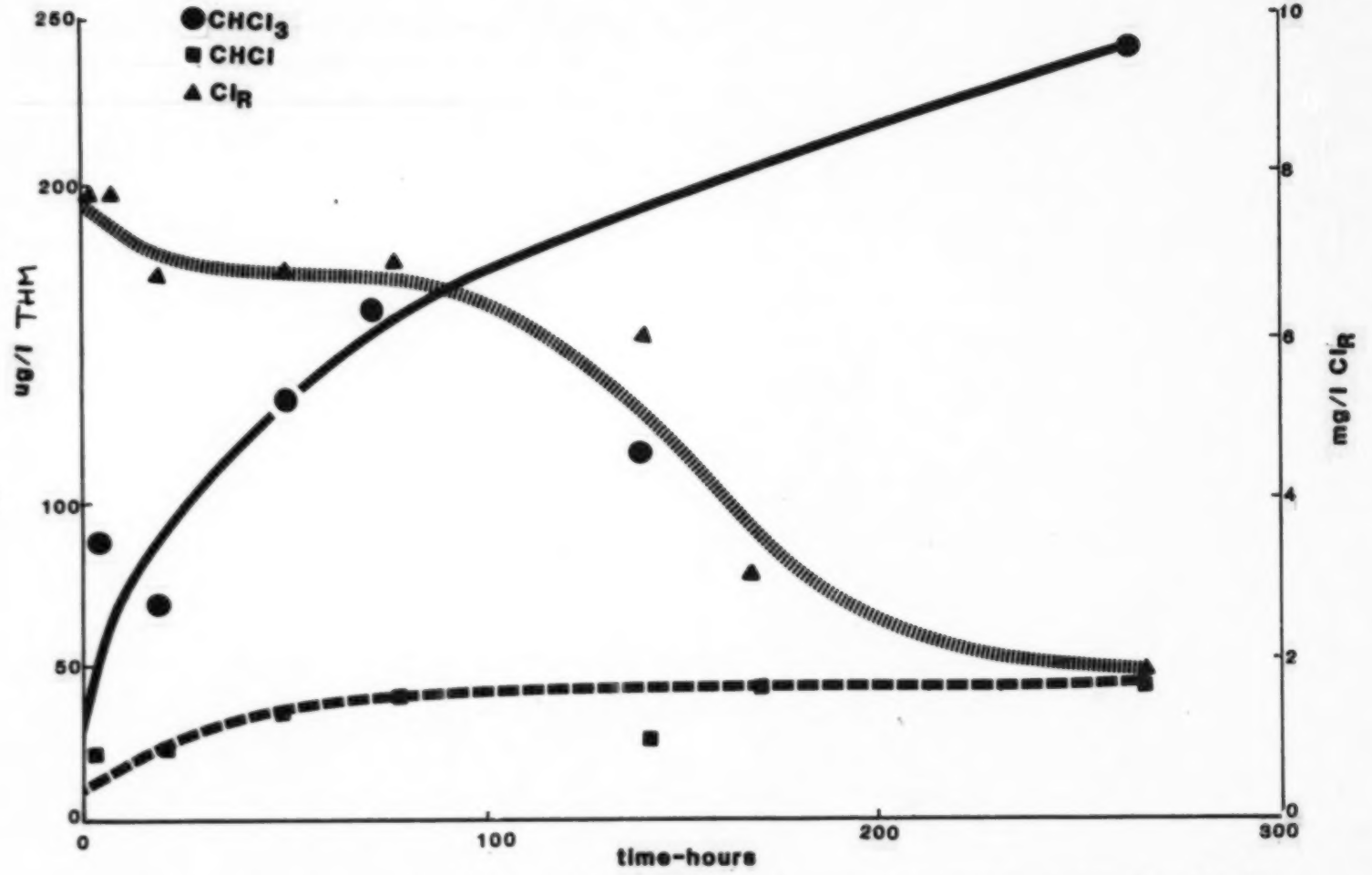

Figure 33. Chlorine residual, chloroform and dichlorobromomethane concentrations in chlorinated Passaic River water at the PVWC treatment plant (Station 100).

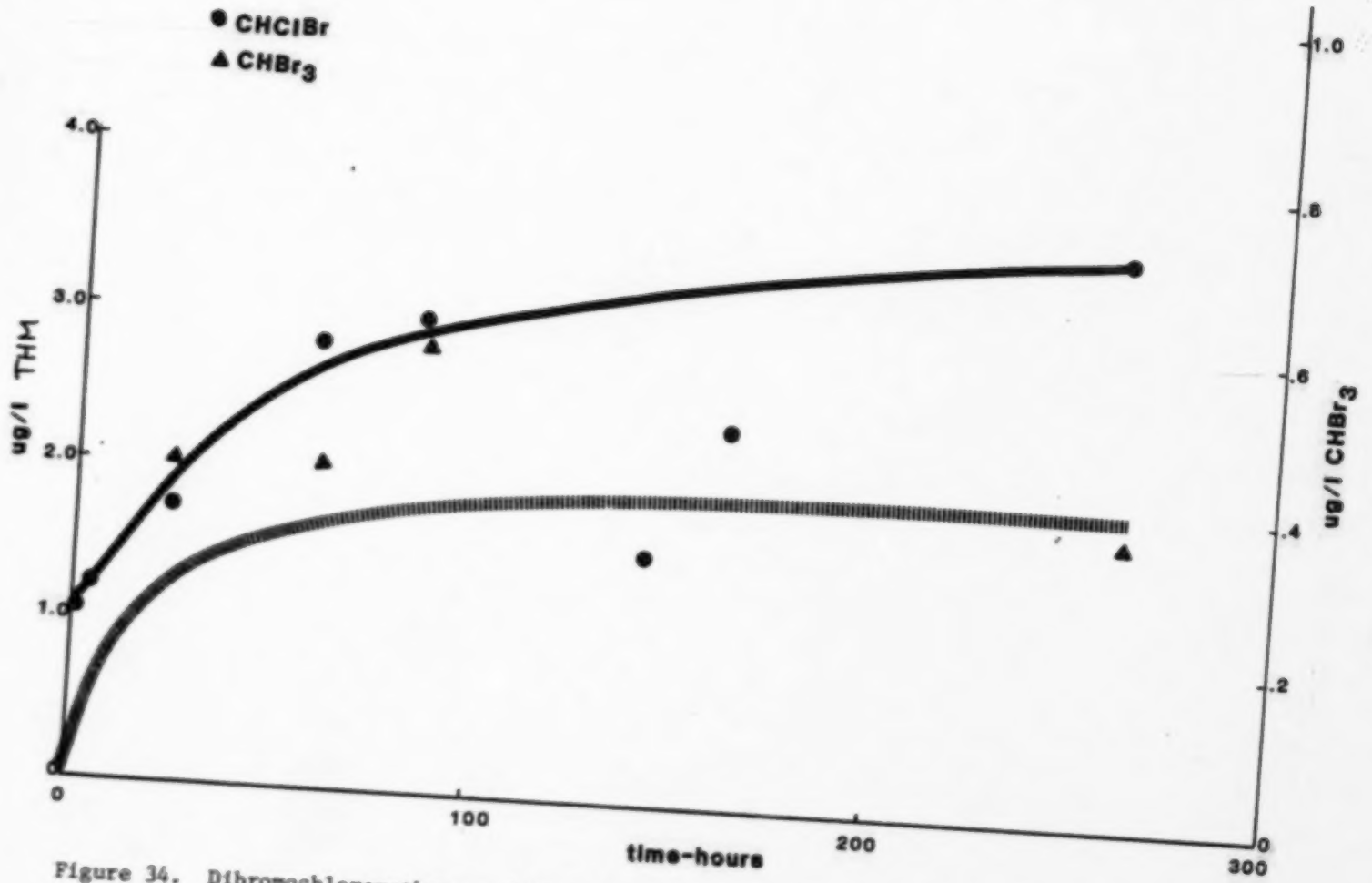

Figure 34. Dibromochloromethane and bromoform concentrations in chlorinated Passaic River water at the PVWC treatment plant (Station 100).

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REFERENCES

Bellar, T. and Lichtenberg, J.J., (1974), The Determination of Volatile Organic Compounds at the ug/L Level in Water by Gas Chromatography. EPA 670/4-74/1009, U.S. Environmental Protection Agency.

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Symons, J.M.; Bellar, T.A.; Carswell, J.K.; DeMarco, J.; Kropp, K.L.; Robeck, G.G.; Seeger, D.R.; Slocum, C.J.; Smith, B.L.; and Stevens, A.A., (1975) National Organic Reconnaissance Survey for Halogenated Organics. Journal of AWWA, 67, 634.

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